SELF-CONSISTENT CLUSTER TREATMENT OF KINETIC
AND MAGNETIC EFFECTS IN NARROW ENERGY BANDS

by

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SELF-CONSISTENT CLUSTER TREATMENT OF KINETIC
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ABSTRACT

A new self-consistent cluster method is developed to account for
electronic motion in narrow energy bands. This technique is first
applied to Hubbard's Hamiltonian with the following results:

1. A Mott insulator-metal transition is observed at values
   of the bandwidth close to theoretical predictions.

2. There also occurs a conductor-conductor transition for
   electronic populations between $0.5 \leq n \leq 1.5$ electrons per site. The
   conductivity suddenly increases past a critical bandwidth.

3. The solid has a magnetic ground state identical with Nagaoka's
   for the F.C.C. and H.C.P. structures. It is non-magnetic for $n \leq 1$
   but totally magnetized for $n \geq 1$.

4. The system has an antiferromagnetic ground state in the
   insulator region ($n = 1$). Its behavior is also antiferromagnetic in
   the conductor region, as testified by its magnetic susceptibility.

5. At constant volume, there is a second order phase transition
   from the magnetic to the non-magnetic state. The susceptibility at
   this point is unconventional. It goes discontinuously to infinity.

6. The constant pressure thermodynamics predict low temperature
   thermal expansion followed by a solid-fluid first order phase
   transition at a critical temperature.

When applied to the Anderson impurity problem, the following
results hold:

1. The s-band density of states is unperturbed except slightly
   at the chemical potential. The chemical potential is then controlled
   solely by the unperturbed s-band.
2. Hopping of the impurity electrons onto the s-band can only occur at the chemical potential.

3. A totally localized moment is found to exist under conditions similar to Anderson's in the ground state.
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CHAPTER I

INTRODUCTION

In the field of Solid-State Physics there has been a tremendous amount of work put into the study of the electronic properties of matter. There are two conventional schools of thought as regards the approach to such studies. On one hand, there is the tight-binding approximation in which the electrons are primarily bound to specific atoms of the solid and all other forms of interatomic interactions are considered as perturbations. On the other hand, there is the itinerant electron approximation in which the electrons are essentially free to move around, due to their kinetic energy, in given energy bands and all forms of two-body interactions (Coulomb interaction) are added as perturbations. Both approaches have their merits in cases where either localized or band properties dominate; but they also have their drawbacks: generally complexity.

There is, however, one scheme which exhibits both simplicity and physical meaning in some specific tight-binding problems; this is the self-consistent cluster approximation\(^1\). This technique was devised for problems where the electrons are so tightly bound to their atoms that there cannot be any hopping. This then justifies treating each atom with a preassigned spin as in atomic theory. The only interaction considered is a scalar spin-spin one of the form \( \hat{S}_i \cdot \hat{S}_j \) (Heisenberg exchange)\(^2\). In this method, one considers a cluster of atoms or equivalently of spins and replaces the coupling between the cluster spins and those of the rest of the system by an
effective coupling to an appropriate spin reservoir or molecular field. The self-consistency part comes in requiring the average behavior of the reservoir coupling quantity to be equal to the average thermodynamic behavior of the equivalent cluster quantity. The simplicity of this method is inherent in the approximation of the solid's behavior by that of a much smaller cluster.

The next step in cluster theory is then to allow for electronic motion, i.e., for the fact that the electrons are not so tightly bound after all, but they can indeed hop from atom to atom. This approach would still benefit from simplicity and it would offer a needed compromise to unavoidable band effects.

This work is a novel extension of the present cluster theories to account for electronic motion in cases where the localized properties of the electrons is still expected to dominate over the band properties.

The formalism will first be developed, in all of its generality, to encompass both the old spin-coupling and the new electron motion problems with emphasis put on the implications of the latter. The body of this thesis will then be devoted to a couple of illustrative applications to solid-state problems. In order to better set out the effect of the proposed approximation to electron correlation, the technique will be restricted to current interest examples where the more familiar spin coupling term is neglected. This allows for a better grasp of the problem and a more straightforward analysis of the results in the light of the proposed approximation to electron correlation.
Fig 2-1  PICTORIAL REPRESENTATION OF THE CLUSTER METHOD FOR THE SIMPLE CUBIC STRUCTURE
CHAPTER II

THE APPROXIMATION

1. A General Crystal Hamiltonian

One of the more popular ways of attacking the many-body problem of electrons in a crystal is that of second quantization. Following the general second quantization rules\(^*\), Hubbard\(^3\) wrote down the non-relativistic electronic Hamiltonian in occupation space using the Wannier representation. It can be rewritten as:

\[
\hat{H} = \sum_{ij} \sum_{\nu} \sum_{\sigma} \epsilon_{ij} a_{i\nu\sigma}^+ a_{j\nu\sigma} + \frac{1}{2} \sum_{ijkl} \sum_{\mu\nu\tau\rho} \sum_{\sigma'} V(i\mu;j\nu;k\tau;l\rho) a_{i\mu\sigma}^+ a_{j\nu\rho}^+ a_{k\tau\sigma'}^+ a_{l\rho\sigma'}
\]

(2.1)

The Fermion operators \(a_{i\nu\sigma}, a_{i\nu\sigma}^+\) respectively destroy and create an electron of spin \(\sigma\) on the \(i^{th}\) atom of the \(\nu\) band. They obey the usual anticommutation rules:

\[
\{a_{i\nu\sigma}, a_{j\mu\sigma}'\} = \delta_{ij} \delta_{\mu\nu} \delta_{\sigma\sigma'}
\]

(2.2)

\[
\{a_{i\nu\sigma}, a_{j\mu\sigma}'\} = \{a_{i\nu\sigma}^+, a_{j\mu\sigma}'\} = 0
\]

\*See Schweber\(^4\).
The first term in Equation (2.1) accounts for the kinetic and crystal potential energies of the electrons. It allows electrons to move from atom to atom within an energy band. The second term accounts for the Coulomb repulsion between the electrons which results in a scattering of two interacting electrons.

2. Narrow Energy Bands

In the case of a very narrow band solid, characterized by small and short-range interatomic terms, the Coulomb interaction term is usually restricted to the direct intra-atomic and the familiar atomic spin exchange terms. These are reasoned to be the larger and controlling elements of the inter-electron interaction. The narrow-band Hamiltonian is then usually:

\[
\mathcal{H} = \sum_{ij} \sum_{\nu} \sigma \Sigma_{i\nu} a_{i\sigma}^{+} a_{j\nu} + \sum_{i\nu} \Sigma_{n\nu} n_{i\nu}^{+} n_{i\nu}^{+} \\
+ \frac{1}{2} \sum_{i\mu \neq \nu} \sum_{\sigma} c_{i\mu \sigma}^{+} a_{i\sigma}^{+} a_{i\sigma} a_{i\sigma}^{+} \\
+ \frac{1}{2} \sum_{i\neq j} \sum_{\mu \nu \sigma} c_{i\mu \sigma}^{+} c_{j\nu \sigma}^{+} a_{i\sigma} a_{j\sigma}^{+}
\]  

(2.3)

The first term again represents the kinetic and crystal energies. It is the presence of the inter-atomic part of this term which is the new addition to cluster theories. It was always neglected previously. The second term represents the Coulomb repulsion energy of two opposite spin electrons when on the same atom and in the same band. The third term involves intra-site inter-band electron exchange whereas the fourth one,
the inter-site, inter- and intra-band electron exchanges.

3. Cluster Theory

The problem is then that of solving or rather approximating a solution to this narrow energy band Hamiltonian. In the spirit of the cluster theories, consider a cluster of atoms or equivalently of sites. Within this group of sites, the electrons can move around because of their kinetic and crystal energy and they can interact with one another through the various Coulomb repulsion and exchange terms determined previously. However the electrons are not conserved within this cluster. Their kinetic and crystal energy allows them to jump from the cluster to the bordering sites outside and vice-versa. Moreover, the inter-site exchange mechanism will couple the electrons on atoms each side of the perimeter of the cluster. This is depicted in the following separated Hamiltonian:

\[
\mathcal{H} = \mathcal{H}_i + \mathcal{H}_o + \mathcal{H}_c
\]

\[
\mathcal{H}_i = \sum_{ij} \sum_{\nu} \Sigma \nu^+ \mathcal{a}^+_i \mathcal{a}_j \mu^+ \mathcal{a}^+_j \mu \mathcal{a}_j + \sum_{\nu} \nu^+ \nu^+ \mathcal{a}^+_i \mathcal{a}_i \nu \mathcal{a}_i \nu
\]

\[
+ \frac{1}{2} \sum_{i} \sum_{\nu} \Sigma C \mu^+ \mathcal{a}^+ \mathcal{a}^+_i \mu \mathcal{a}_i \mu \mathcal{a}_i \mu
\]

\[
+ \frac{1}{2} \sum_{i} \sum_{\nu} \Sigma J(i; j) \mathcal{a}^+_i \mathcal{a}^+_j \mathcal{a}_i \mathcal{a}_j \mu \mathcal{a}_i \mathcal{a}_j \mu
\]
\[ \mathcal{H}_o = \sum_{\alpha \gamma \nu} \sum_{i,j} T_{ij} a^+_{\alpha \nu} a_{\gamma \nu} + \sum_{\alpha \nu} \sum_{\alpha^+} n_{\alpha \nu} n_{\alpha^+} \]

\[ + \frac{1}{2} \sum_{\alpha \mu \gamma} \sum_{\sigma \sigma'} \sum_{\nu} C_{\alpha \mu \nu} a^+_{\alpha \mu \nu} a_{\gamma \nu} a_{\mu \sigma} a_{\nu \sigma} \]

\[ + \frac{1}{2} \sum_{\alpha \mu \gamma} \sum_{\sigma \sigma'} \sum_{\nu} J(\alpha \mu ; \gamma \nu) a^+_{\alpha \mu \nu} a_{\gamma \nu} a_{\mu \sigma} a_{\nu \sigma} \]

\[ \mathcal{H}_c = \sum_{\lambda \delta} \sum_{\nu} \sum_{\sigma} T_{\lambda \delta} (a^+_{\lambda \nu} a_{\delta \nu} + a^+_{\delta \nu} a_{\lambda \nu}) \]

\[ + \frac{1}{2} \sum_{\lambda \delta} \sum_{\nu} \sum_{\sigma} J(\lambda \mu ; \delta \nu) a^+_{\lambda \mu \nu} a_{\delta \nu} a_{\lambda \nu} a_{\mu \delta} \]

The latin subscripts refer to sites within the cluster and the greek ones, to sites outside.

What is sought is a way to pull the cluster out of its environment and replace the severed links between it and its surroundings by ones to electron reservoirs. These reservoirs would then be substituting for the effect of the solid outside the cluster. One such a reservoir would have to be able to give and take electrons from the cluster in order to preserve the physical picture of electrons being constantly transferred to the outside (electron removed) or from the outside (electron added). The other type of reservoirs would be those needed to preserve the idea of electron exchange between the cluster and its neighborhood. This idea is schematically depicted in Figure 2.1.

Conventionally, the cluster technique consists in thermodynamically averaging over the operators outside the cluster. Those averages that are
foreign to the cluster can be regarded as cluster constants and simply dropped. Doing just this, the resulting tentative cluster Hamiltonian would be:

$$\mathcal{H}_{cl} = \mathcal{H}_i + \mathcal{H}_c$$  \hspace{1cm} (2.5)

where

$$\mathcal{H}_c = \Sigma \Sigma \Sigma \Sigma \Sigma (a_{\mu \nu \sigma}^+ a_{\delta \nu \sigma}^+ a_{\delta \nu \sigma} a_{\mu \nu \sigma})$$  \hspace{1cm} (2.6)

$$- \frac{1}{2} \Sigma \Sigma \Sigma \Sigma \Sigma \Sigma \Sigma (a_{\mu \nu \sigma} a_{\lambda \mu \sigma} a_{\lambda \mu \sigma} a_{\lambda \mu \sigma}^+ a_{\delta \nu \sigma}^+ a_{\delta \nu \sigma}^+ a_{\delta \nu \sigma})$$

The \(<---\) terms imply a thermodynamic average. The intrinsic part \(\mathcal{H}_i\) is left intact since it involves only internal energies whereas the hopping and exchange between the cluster and its surroundings are replaced by appropriate reservoir terms in \(\mathcal{H}_c\). It is these reservoirs which preserve the physics of the cluster.

1. That part of \(\mathcal{H}_c\) which involves the term

$$- \frac{1}{2} \Sigma \Sigma \Sigma \Sigma \Sigma \Sigma \Sigma (a_{\mu \nu \sigma} a_{\delta \nu \sigma}^+ a_{\delta \nu \sigma} a_{\delta \nu \sigma}^+ a_{\mu \nu \sigma}^+ a_{\delta \nu \sigma}^+ a_{\delta \nu \sigma})$$

i.e., the exchange between like-spin electrons, is the familiar molecular field approximation. The \(<n_{\alpha \nu \sigma}>\) average acts like a magnetic field trying to line up the bordering cluster electrons with it. This field is usually thought of representing the average effect of the rest of the system on the cluster in conventional Heisenberg-type exchange cluster problems. In fact Hubbard's crystal field approximation (3) is that of a single site cluster with only this part of \(\mathcal{H}_c\) considered.

2. The hopping between the cluster and the immediate neighborhood has been replaced by Fermion source terms which can create or anihilate electrons
in the cluster. The rest of the system has been replaced by electron reservoirs which preserve the idea of electrons constantly appearing and vanishing from the cluster. It is this new concept in cluster theories which will allow electron correlation to be preserved between the cluster and its surroundings. However this was done at a cost. As was mentioned before, the electron operators anticommute with one another. This is required to antisymmetrize the wave function. Thus, the only way a pair of operators like \( a_{k\nu\sigma}^+ a_{\delta\nu\sigma}^- \) could be bluntly factored into \( a_{k\nu\sigma}^+ <a_{\delta\nu\sigma}^- \) without any a priori knowledge of the distribution of all the other electrons is by the tacit assumption these operators commute. This means the anticommutation requirement between the cluster electrons and those of the rest of the system has been implicitly lifted. Although the cluster wave function will be properly antisymmetrized, since the anticommutation property has been preserved within the cluster, the system's wave function will be a symmetric arrangement of the cluster and the external system's wave functions. As a matter of fact, this loose use of the anticommutation rules is implicit in all molecular field and Hartree-Fock type approximations. Just how drastic this result is on electron correlation is difficult to assess. It is only by studying the effect on test problems that this can be evaluated.

As was pointed out previously and is now very evident, the cluster does not conserve particles. This implies particle fluctuations and as such canonical statistics\(^*\) can no longer be used for the cluster statistics.

\* See Huang (5).
Grand canonical statistics* must be used. A chemical potential must then be introduced into the problem. The cluster Hamiltonian, in its final form, is then

\[ H_{cl} = H_1 + H_{c} + \mu \sum_{i \nu} \sum_{\sigma} \epsilon_{i \nu \sigma} \]  \hspace{1cm} (2.7)

It is this chemical potential \( \mu \) which will allow control over the average number of particles in the cluster. This turns out to be a tremendous advantage over previous cluster theories in that the number of electrons is no longer fixed to an integral number per atom. This, indeed, takes the problem closer to real solids' behavior. This non-conservation of particles as typified by the Fermion source terms will then have the effect of coupling cluster states differing by one electron. The cluster eigenstates will no longer be eigenstates of the number operator.

Now what about this average \( \langle a_{i \nu \sigma}^\dagger \rangle \)? What is implied by it? This whole approximation scheme rests on giving this average meaning. Surely it is not a physical quantity, it cannot be "seen" or measured experimentally. The system's Hamiltonian conserves particles and as such \( \langle a_{i \nu \sigma}^\dagger \rangle \) would be identically zero in the real system since it is a thermodynamic average. However in the context of a cluster it does take on meaning. The number of particles is not conserved within the cluster and it should be possible to conceive of a certain likelihood \( \langle a_{i \nu \sigma}^\dagger \rangle \), \( \langle a_{i \nu \sigma} \rangle \) of an electron being transferred in or out of the cluster, i.e., of adding or removing an electron.

* See Huang (5).
The existence of \( <a_{i\nu}^+ > \) is then contingent on the existence of a cluster and is intimately associated to electron fluctuations. To concretize this concept, let us look at the equation relating the time behavior of the average number of electrons in the cluster

\[
\frac{\partial}{\partial t} <n_{c\ell} > = <[n_{c\ell}, \hat{H}_{c\ell}]> 
\]

\[= \sum \Sigma \Sigma T_{\ell \delta}^\nu (\langle a_{\ell \nu}^+ \rangle <a_{\delta \nu}^- > - <a_{\delta \nu}^+ > <a_{\ell \nu}^- > )^* \]

\[= \text{flow of particles in} - \text{flow of particles out} \]

At thermodynamic equilibrium, \( \frac{\partial}{\partial t} <n_{c\ell} > = 0 \). The flow of electrons in and out of the cluster is then \( \Sigma \Sigma T_{\ell \delta}^\nu (a_{\ell \nu}^+ <a_{\delta \nu}^- > - <a_{\delta \nu}^+ > <a_{\ell \nu}^- > ) \). This electron flow is then wholly dependent on these creation and destruction operator averages. This again emphasizes their close association to the motion of electrons in and out of the cluster.

3. The remaining part of \( \hat{H}_{c\ell} \), i.e.,

\[- \frac{1}{2} \Sigma \Sigma \Sigma J(k \mu ; \delta \nu) a_{k \mu}^+ a_{k \mu} - \langle a_{\delta \nu}^- a_{\delta \nu}^- > \]

pertains to the exchange of two opposite spin electrons. The effect of the system external to the cluster is then to introduce a spin flipping term in the cluster Hamiltonian. This is still an unconventional cluster term but, like the hopping term, it has a right to its own existence. The consequence of such a reservoir term would be to produce a non-conservation of spin within the cluster.

\[\]

*This expression is the isotropic form of the current operator in Appendix F.*
But this effect also follows particle non-conservation and so it is easier to accept this fact. Again this average only exists in the cluster context since the real Hamiltonian conserves spin. It is then closely associated with total spin fluctuations in the cluster. Whether or not one should retain this term in the presence of the direct molecular field term is a question pertaining to the order of the approximation.

4. **Self-Consistency and Thermodynamics**

Now that an effective Hamiltonian has been derived which has all the appearance of preserving the intrinsic physics of the problem, there is a need to define the self-consistency conditions by which all of the reservoir or field terms can be uniquely determined. This is simple and follows directly the lines of conventional cluster theories. These averages should be set equal to their cluster counterparts. The following self-consistency rules are then proposed:

\[ \langle n_{\delta\nu\sigma} \rangle = \langle n_{\lambda\nu\sigma} \rangle \]  \hspace{1cm} (2.9)

\[ |\langle a_{\delta\nu\sigma} \rangle| = |\langle a_{\lambda\nu\sigma} \rangle| \]

\[ |\langle a_{\delta\nu\sigma}^+ a_{\delta\nu-\sigma} \rangle| = |\langle a_{\lambda\nu\sigma}^+ a_{\lambda\nu-\sigma} \rangle| \]

All the averages with the \( \lambda \) subscript are grand canonical thermodynamic cluster averages.

\[ \langle \Theta \rangle = \frac{\text{Tr}(e^{-\beta \mathcal{H}_{\text{cl,0}}})}{\text{Tr} e^{-\beta \mathcal{H}_{\text{cl}}}} = \frac{\sum_{\psi} \langle e^{-\beta \mathcal{H}_{\text{cl,0}}} | \psi \rangle}{\sum_{\psi} \langle e^{-\beta \mathcal{H}_{\text{cl}}} | \psi \rangle} \]  \hspace{1cm} (2.10)
These averages are best performed in the diagonal representation in which

$$\mathcal{H}_{\text{cl}} |\psi_a\rangle = E_a |\psi_a\rangle$$  \hspace{1cm} (2.11)

which implies solving the secular equation for the cluster Hamiltonian.

The absolute value on the two unconventional reservoir terms comes from the fact the averages involved are not physical quantities, and as such, cannot be assigned a definite phase.

The thermodynamics of the cluster are then solved in the usual way by calculating all interesting averages $<\Theta>$ as in Eq. (2.10).

5. Further Comments on the Electron Correlation

Now that the physics of the approximation have been well described, let us examine some further particularities of the electron correlation reservoir. The first one concerns the range of the electron hopping involved. As was pointed out earlier, the averages $<a_{+}^{\delta_{\text{uo}}} a_{\delta_{\text{uo}}}^{\delta_{\text{uo}}} >$ between the cluster and its neighborhood has been approximated by $<a_{+}^{\delta_{\text{uo}}} a_{\delta_{\text{uo}}}^{\delta_{\text{uo}}} >$. But this was done without any explicit consideration of the range of this hopping that is the distance $(\overline{R}_{\ell} - \overline{R}_o)$ between the atoms involved in the transfer. This is evident in the self-consistency condition. This is definitely drastic especially as $|\overline{R}_{\ell} - \overline{R}_o|$ increases since it is shown in Appendix A that

$$\lim_{|\overline{R}_{\ell} - \overline{R}_o| \to \infty} <a_{+}^{\delta_{\text{uo}}} a_{\delta_{\text{uo}}}^{\delta_{\text{uo}}} > = 0.$$  \hspace{1cm} This approximation is then only justifiable

for short range hopping such as nearest neighbor hopping. As it turns out, this restriction is not drastic since that is a normal procedure in tight
binding calculations.* Nearest neighbor hopping usually contributes the overwhelming part to the hopping energy in narrow energy bands.

Another point worth bringing up is the fact that the approximation to the hopping term is not unique. This is a consequence of neglecting the anticommutation of the cluster electrons with the others. In the original Hamiltonian, Equation 2.4, the hopping between the cluster and its surroundings in $\mathcal{H}_c$ could well have been written in the form:

$$
\sum \sum \sum \left( a_{\nu}^{\dagger} a_{\nu} - a_{\nu}^{\dagger} a_{\nu} \right)
$$

(2.12)

by making use of the anticommutation rules. Under the cluster approximation scheme this term would become

$$
\sum \sum \sum \sum \left( a_{\nu}^{\dagger} a_{\nu} - a_{\nu}^{\dagger} a_{\nu} \right)
$$

(2.13)

which differs from the previous corresponding term in $\mathcal{H}_c$ by the minus sign.

The question then arises as to which form to use? This can be settled by making the natural requirement that the effective cluster Hamiltonian matrix be hermitian. This implies that if $\{ \psi_\alpha \}$ is a complete set of states

$$
\langle \psi_1 | \mathcal{H}_{cl} | \psi_2 \rangle = \langle \psi_2 | \mathcal{H}_{cl} | \psi_1 \rangle^* 
$$

In particular if $| n \rangle$ is a state of the cluster with $n$ electrons in it, since $\mathcal{H}_{cl}$ no longer conserves particles there would be some matrix elements satisfying:

*See Kemeny(6) for instance.
\[ <n | H_{cl} | n+1> = <n+1 | H_{cl} | n> \]

Substituting for \( H_{cl} \):

\[
< n | H_{cl} | n+1> = \sum_{\ell \delta} \sum_{\nu} \varepsilon T_{\ell \delta}^{\nu} < a_{\delta \nu}^{+} | n | a_{\ell \nu} | n+1 >
\]

\[
< n+1 | H_{cl} | n> = \sum_{\ell \delta} \sum_{\nu} \varepsilon T_{\ell \delta}^{\nu} < a_{\delta \nu}^{+} | n+1 | a_{\ell \nu} | n>
\]

\[ 2^{nd} \text{ form} \]

\[
< n | H_{cl} | n+1> = -\sum_{\ell \delta} \sum_{\nu} \varepsilon T_{\ell \delta}^{\nu} < a_{\delta \nu}^{+} | n | a_{\ell \nu} | n+1 >
\]

\[
< n+1 | H_{cl} | n> = -\sum_{\ell \delta} \sum_{\nu} \varepsilon T_{\ell \delta}^{\nu} < a_{\delta \nu}^{+} | n+1 | a_{\ell \nu} | n>
\]

\[ 2^{nd} \text{ form} \]

The hermiticity condition is then satisfied if

\[
< a_{\delta \nu}^{+} > = < a_{\delta \nu} >^{*}
\]

\[ 1^{st} \text{ form} \]

\[
< a_{\delta \nu}^{+} > = -< a_{\delta \nu} >^{*}
\]

\[ 2^{nd} \text{ form} \]

However if \( H_{cl} \) is, indeed, hermitian this would imply that for any operator \( \theta \)

\[ < \theta^{+} > = < \theta >^{*} \]

The first form is then consistent with this requirement whereas the second form is not. In order to make the second form hermitian, one needs impose a non-hermitian condition. This second form is then unnatural and warrants the use of the original form.
6. **Alternate Derivation of the Cluster Hamiltonian**

Let us now look at a more mathematical derivation of the cluster Hamiltonian. This approach will be useful when studying the electrical properties of the cluster. The basic cluster approximation can be considered as that of writing the total eigenstate $|\psi_a\rangle$ of the system as a tensor product over cluster eigenstates $|\psi_{ia}\rangle$ where $i$ represents a given cluster.

$$|\psi_a\rangle = \bigotimes_i |\psi_{ia}\rangle$$  \hspace{1cm} (2.14)

These cluster eigenstates satisfy

$$\mathcal{H}_{icl} |\psi_{ia}\rangle = E_a |\psi_{ia}\rangle$$  \hspace{1cm} (2.15)

where $\mathcal{H}_{icl}$ is the still to be defined cluster Hamiltonian. A thermodynamic average $\langle \Theta \rangle$ then becomes, under the tacit neglect of the inter-cluster anti-commutation rules:

$$\langle \Theta \rangle = \frac{\text{Tr} \ e^{-\beta \mathcal{H}_{icl}}} {\text{Tr} \ e^{-\beta \mathcal{H}_{icl}}}$$  \hspace{1cm} (2.16)

$$= \sum_{\alpha} \left( \sum_{i} e^{-\beta \mathcal{H}_{icl}} |\psi_{ia}\rangle \langle \psi_{ia}| \right) \langle \Theta \rangle$$

The effective cluster Hamiltonian is defined as
\[ \mathcal{H}_{\text{icl}} = \frac{\sum_{\alpha l} \langle \psi_{j\alpha} | e^{-\beta \mathcal{H}_{\text{jcl}}} \mathcal{H} \langle \psi_{l\alpha} \rangle \rangle_{\psi_{j\alpha}}}{\sum_{\alpha j} \langle \psi_{j\alpha} | e^{-\beta \mathcal{H}_{\text{jcl}}} \mathcal{H}_{\text{jcl}} \psi_{j\alpha} \rangle_{\psi_{j\alpha}}} \]  

(2.17)

It is easily seen that our narrow band cluster Hamiltonian would be:

\[ \mathcal{H}_{\text{icl}} = \mathcal{H}_{1} + \langle \mathcal{H}_{0} \rangle + \mathcal{H}_{c} \]

as before and the thermodynamics would be the same.
CHAPTER III

THE PROBLEMS

There are two interesting problems which are particularly well suited to this new cluster approach to electron correlation and which are of fundamental interest. These shall now be described.

1. Hubbard's Hamiltonian (7)

1.1. The hamiltonian

The system Hubbard originally set out to study is that of a single band solid where the two largest terms contributing to the energy are due to the motion of electrons from atom to atom and to Coulomb repulsion of opposite-spin electrons on the same atom. The effect of all other forms of electronic interactions was neglected compared to the effect of these two terms. In short, out of the narrow band Hamiltonian in Equation (2.3) he considered only the first two terms and restricted them to a single band. His Hamiltonian is then written as:

$$H = \sum_{ij} E_{ij} a_{i}^{+} a_{j} + \sum_{i} E_{n_{i}^{+} n_{i}^{+}}$$  \hspace{1cm} (3.1)

The reason this Hamiltonian is appealing dates back to an age old quest for a better understanding of ferromagnetic materials. These materials are characterized by partly filled d-bands and although these bands are appreciably wide, these substances exhibit an astonishing amount of atomic-like behavior. It is then obvious the behavior of these solids is governed by atomic properties. But how do the band properties affect them? Hubbard
was then looking for a theory of correlations which would adequately account for the atomistic nature of the solids. In order to have a substance behave in an atomic way, in spite of the electronic motion in the d-band, he reasoned that the electrons on an atom should be strongly correlated with each other, but only weakly with electrons on other atoms. As borne out by Hund's rules, there must be a strong intra-atomic interaction which, when an atom has an electron of a given spin on, will repel opposite spin electrons. If this interaction is strong enough, then it is plausible the electron motions will be correlated in much a way to keep a preponderance of the same spin on an atom and thus yielding atomic-like behavior. The Hamiltonian Hubbard proposed in Equation (3.1) would then contain the essentials of the above arguments. It would be a simple, approximate model for the effects of correlation phenomena. Since this Hamiltonian presumably contains the essentials of atomic-like behavior, one then wonders if this correlation model could not perhaps give rise to ferromagnetism. It has been generally accepted that it is spin exchange which is responsible for ferromagnetism. This would then be a great opportunity to study the effects of electron correlation only and see if it could not lead to magnetic ordering.

1.2 Cluster approximation

As has been pointed out in Section II.5 our cluster approximation should be restricted to nearest neighbor hopping problems only, at little sacrifice to generality. The cluster approximation to Hubbard's Hamiltonian would then be (Eq. 2.7)
\[ H_{cl} = \sum_{i j \sigma}^n \varepsilon_{i j \sigma} a_{i j \sigma}^+ a_{i j \sigma} + \sum_{i}^{n} \mu_i \varepsilon_{i \sigma} n_{i \sigma} \]

\[ + \sum_{\delta} \sum_{\delta} \left( a_{\delta \sigma}^+ <a_{\delta}^- > + <a_{\delta}^+ a_{\delta \sigma}^- > \right) \]

The addition of the chemical potential is a necessary step to allow for density fluctuations within the cluster.

1.3 **Symmetry Breaking Properties**

It will prove well worth while to take a second look at the approximation and deduce any symmetry properties that are particular to it.

A. **Spin Symmetry**

Looking at the full Hamiltonian (3.1), it is obvious that it is invariant under any rotation of the axis of electron spin quantization (see Appendix B). However, this is no longer true of the cluster Hamiltonian. The part of this cluster Hamiltonian which involves only the internal energy and motion:

\[ \sum_{i j \sigma}^n \varepsilon_{i j \sigma} a_{i j \sigma}^+ a_{i j \sigma} + \sum_{i}^{n} \mu_i \varepsilon_{i \sigma} n_{i \sigma} \]

is, of course, invariant. It is the part involving the reservoirs which is not. To show this, let us perform the following transformation on the reservoir coupled operators:

*One need not approach the problem using this particular description. Exactly equivalent results will be obtained by simply setting up the energy matrix arising from the cluster Hamiltonian and performing the unitary transformation described in (3.3) on this matrix.*
\[ Ra_{\pm} R^+ = \frac{(<a_{\delta^+}, a_{\pm^+}, + a_{\delta^+}^+ a_{\pm^+})}{Q_\delta} \]  
\[ Ra_{\pm} R^+ = \frac{(<a_{\delta^+}, a_{\pm^+}, - a_{\delta^+}^+ a_{\pm^+})}{Q_\delta} \]

\[ Q_\delta = \sqrt{|<a_{\delta^+}|^2 + |<a_{\delta^+}^+>|^2} \]

This is a perfectly legitimate transformation under rotation as per Appendix B. A typical term then becomes

\[ RT[<a_{\delta^+}^+ a_{\pm^+} + <a_{\delta^+}^+ a_{\pm^+}>] R^+ = TQ_\delta a_{\pm^+} \]  
(3.4)

The transformed cluster Hamiltonian is then

\[ R \mathcal{H}_{cl} R^+ = \mathcal{H}_{cl}' = \sum_{\delta} T \mathcal{E} Q_\delta (a_{\pm^+}^+ + a_{\pm^+}) \]  
(3.5)

\[ + T \sum_{\delta} \sum_{\sigma, \sigma'} a_{\delta}^+ a_{\sigma} a_{\sigma'} + I \sum_{\delta} I_{\delta} a_{\delta}^+ n_{\delta} \]  
\[ - \mu \sum_{\delta} \sum_{\sigma} n_{\delta} \sigma \]  

Since this modified form does not allow any hopping of down spin electrons in and out of the rotated cluster, \(<a_{\pm^+}> \equiv 0\). But then, the self-consistency condition requires

\[ |<a_{\delta^+}| = |<a_{\pm^+}| = |<Ra_{\pm} R^+| \]  
(see Appendix C)

\[ = |<a_{\delta^+} a_{\pm^+} + a_{\delta^+}^+ a_{\pm^+}>| Q_\delta \]  
\[ = |<a_{\delta^+}^+ a_{\pm^+}| Q_\delta \]  

\[ = |<a_{\delta^+}>| |<a_{\pm^+}| Q_\delta \]
or
\[ Q_\delta = | <a_{i+}^+, > | \tag{3.6} \]

The same is true of the down spin self-consistency condition. The cluster Hamiltonian can finally be rewritten as:

\[ \mathcal{H}_{cl}^t = T \sum_{\delta L} nn \langle a_{i+}^-, a_{i+}^+ \rangle + T \sum_{ij} \Sigma a_{i+}^+, a_{j+}^- \tag{3.7} \]

\[ + I \sum_{i} n_{i+}, n_{i+}', -m \sum_{i} \Sigma n_{i+}' \]

without any knowledge of past history of the cluster.

This special rotation gives considerable insight into the approximation:

1. It shows that the spin symmetry is broken. This is a consequence of neglecting the anticommutation rules between the cluster and its environment. \( S^2 \) is no longer conserved and neither is the number of particles.

2. It shows that any possible reservoir configuration can always be brought to the last form (3.7) where there is only one spin hopping in and out of the cluster. As shown in Appendix C, all these configurations are equivalent, thermodynamically speaking, since they all are rotated forms of the same Hamiltonian. Thus only this last form need be solved. This has the great advantage that only a single reservoir need be determined self-consistently instead of two as in the general case.

The drawback to such a property is that the approximation favors a broken spin symmetry state, i.e., it magnetically biases the system. This
is not detrimental if it is indeed magnetic, but is so for a non-magnetic system.*

B. Time-Reversal Symmetry

Whereas the original Hamiltonian is time reversal invariant as shown in Appendix B, the cluster Hamiltonian surely is not. This follows from the broken spin symmetry. The time reversal operator rotates spins by $180^\circ$ and this spin symmetry must exist if time reversal symmetry is also to exist.

2. Anderson's Hamiltonian

2.1. The Hamiltonian

Anderson has discussed the problem of magnetic impurities dissolved in a non-magnetic host metal. Under certain circumstances these impurities are experimentally found to display the characteristics of a localized moment. This is in spite of the interaction between the impurity electrons and the host metal atoms which results in electrons wishing to migrate to and from the impurity atom. Again this problem bears close similarity to Hubbard's and it can be argued that this localized moment probably results from a strong intra-impurity interaction which would repel opposite spin electrons. The natural way to tackle the electron correlation problem of these impurities would then be to look at the following Hamiltonian:

*Such a polarized hopping approach to Hubbard's Hamiltonian was tried by M.C. Gutzwiller(8), and it yielded a magnetic ground state in some cases.
\[ H_c = \sum_{k_\sigma k_{\sigma'}} E_{k_\sigma} n_{k_{\sigma} \sigma} + \sum_{o_\sigma} n_{o_\sigma} + E_o \sum_{o_\sigma o_{\sigma'}} n_{o_\sigma} n_{o_{\sigma'}} \]

\[ + \sum_{k_\sigma} \sum_{k_{\sigma'}} V_k (a_{k_\sigma}^+ a_{k_{\sigma'}} + a_{k_{\sigma'}}^+ a_{k_\sigma}) \]

(3.8)

The first term represents the unperturbed energy in \( k \)-space of the host metal electrons which are assumed to be \( s \)-band electrons. The second and third terms would represent the impurity's unperturbed energy. The last term represents the tendency for electrons to move on and off the impurity to and from the \( s \)-band. As can easily be seen this Hamiltonian has all the essentials of Hubbard's 1. a strong repulsion for opposite spin electrons on the impurity, 2. a kinetic energy coupling between the impurity and the \( s \)-band. Both were looking for the effect of correlation on the atomistic behavior of these systems.

Again one may wonder as to the magnetic implications of the electron correlation in the impurity problem. Is it responsible for the magnetic moments sometimes observed with these impurities? This Hamiltonian was an occasion to find out.

2.2 Cluster approximation

Obviously, Anderson's Hamiltonian is nowhere close to the one used to illustrate the cluster technique in Chapter II. However, this shows the great flexibility of this theory since it can be easily adapted to this new problem. Our objective is to simply find what the cluster technique leads to.

The physical and thermodynamic ideas can be carried forth from Chapter II with some slight adaptive variations. Whereas in the previous case the size of the cluster was arbitrary, it is unambiguously dictated in this one
by the special form of this Hamiltonian. The impurity must be uncoupled from the s-band and this can only be achieved if the impurity is itself the whole cluster. This is intrinsically a single-site cluster problem. Applying the rules of cluster averaging, there are now two distinct uncoupled Hamiltonians. That for the impurity

\[ \mathcal{H}_I = \text{In}_o \Sigma n_o^+ - (E_o + \mu) \Sigma n_{oo} \]

\[ + \Sigma \Sigma V_{K\sigma} (a_{K\sigma}^+ a_{oo}^+ a_{oo}^+ a_{K\sigma}^-) \]

and that for the s-band electrons

\[ \mathcal{H}_S = \Sigma \Sigma (E_{K\sigma} - \mu) n_{K\sigma} + \Sigma \Sigma V_{K\sigma} (a_{K\sigma}^+ a_{oo}^+ a_{oo}^+ a_{K\sigma}^-) \]

Again the chemical potential is added because of the non-conservation of electrons in both sub-Hamiltonians. It allows a control over the total number of particles.

This departure from conventional cluster theory is required since the cluster (i.e. the impurity) no longer behaves anything like the rest of the system (s-band). One can no longer have the whole system's behavior reflected by the cluster's. Both of the uncoupled parts must be dealt with in a coherent way.

As for the translationally invariant crystal, again the physics is preserved. The notion of electrons being added or removed from the impurity and the s-band is still obvious. The reservoir averages can still be related to the non-conservation of electrons in the cluster impurity and in the
s-band, i.e., to the electron flow between the two.

However, the self-consistency condition is not as obvious as before. Actually, there are not one, but two such conditions. One on each of the uncoupled Hamiltonians. The values of the reservoir averages appearing in both Hamiltonians must be equal to the same thermodynamic averages resulting from the solution of both systems:

\[(\sum_{k} \langle a_{k\sigma}^+ \rangle) \text{ used in } \mathcal{H}_I \quad (3.11)\]

\[= (\sum_{k} \langle a_{k\sigma}^+ \rangle) \text{ from the thermodynamic solution of } \mathcal{H}_S \]

\[\langle a_{\sigma\sigma}^+ \rangle \text{ used in } \mathcal{H}_S = \langle a_{\sigma\sigma}^+ \rangle \text{ from the thermodynamic solution of } \mathcal{H}_I \]

Fortunately it will shortly be shown that these two conditions effectively reduce to one.

2.3 Symmetry breaking properties

The cluster approximation to Anderson's Hamiltonian has the same symmetry breaking properties as Hubbard's.

A. Spin Symmetry

As shown in Appendix D, the Anderson Hamiltonian is invariant under spin rotation. This is lost in the approximation. Although the terms independent of the reservoir

\[n_{o\uparrow} n_{o\downarrow}; \sum_{\sigma} n_{\sigma\sigma}; \sum_{\sigma} \Sigma_{k\sigma}\]

are invariant, the reservoir terms are not. To show this, the following special rotation will be performed
\[ R_{a_0^+}^+ = (\Sigma V_k <a_{k^+}^+ | a_{o^+}^+ > + \Sigma V_k <a_{k^+}^+ | a_{o^+}^+ >) / Q \]  (3.12)

\[ R_{a_0^+}^+ = (\Sigma V_k <a_{k^+}^+ | a_{o^+}^+ > - \Sigma V_k <a_{k^+}^+ | a_{o^+}^+ >) / Q \]

\[ Q = \sqrt{|\Sigma V_k <a_{k^+}^+ | a_{o^+}^+ >|^2 + |\Sigma V_k <a_{k^+}^+ | a_{o^+}^+ >|^2} \]

A typical term in \( \mathcal{H}_I \) becomes

\[ R \Sigma \Sigma V_k <a_{k^+}^+ | a_{o^+}^+ > R_{o^+}^+ = Qa_{o^+}^+ \]  (3.13)

Consequently

\[ \mathcal{R} \mathcal{H}_I R_{o^+}^+ = \mathcal{H}_I = I n_{o^+} n_{o^+} -(E_{o^+} + \mu) E n_{o^+} + Q(a_{o^+}^+ + a_{o^+}^+)(a_{o^+}^+ + a_{o^+}^+) \]  (3.14)

Now obviously \( <a_{o^+}^+ > \equiv 0 \) since \( \mathcal{H}_I \) does not allow any down-spin hopping.

Thus, from Appendix C,

\[ <a_{o^+}^+ > = <R_{a_0^+}^+ > = \Sigma V_k <a_{k^+}^+ | a_{o^+}^+ > / Q \]  (3.15)

\[ <a_{o^+}^+ > = <R_{a_0^+}^+ > = \Sigma V_k <a_{k^+}^+ | a_{o^+}^+ > / Q \]

If the same rotation is performed on \( \mathcal{H}_S \),

\[ R_{a_k^+}^+ = ((\Sigma V_k, <a_{k^+}^+ > a_{k^+}^+ )^a_k^+ + (\Sigma V_k, <a_{k^+}^+ > a_{k^+}^+ )^a_k^+) / Q \]  (3.16)

\[ R(a_{k^+}^+ )^a_k^+ = ((\Sigma V_k, <a_{k^+}^+ > a_{k^+}^+ )^a_k^+ - (\Sigma V_k, <a_{k^+}^+ > a_{k^+}^+ )^a_k^+) / Q \]
Substituting for \( <a_{o^+}^+> \), a typical term becomes

\[
R \Sigma <a_{o^+}^+> a_{K^0}^{-} R^+ = <a_{o^+}^+> a_{K^+}^{*}
\]

(3.17)

and so

\[
R H_S R^+ = H'_S = \Sigma \Sigma (e_{K^+} - \mu) n_{K^0} + \Sigma V_K <a_{o^+}^+> a_{K^+}^{*} + <a_{o^+}^+> a_{K^+}^{*}
\]

(3.18)

Moreover, since \( <a_{K^+}^+> \equiv 0 \), from Appendix C,

\[
<a_{K^+}^+> = <Ra_{K^+} R^+> = (\Sigma V_K <a_{K^+}^+>) <a_{K^+}^+>/Q
\]

(3.19)

\[
<a_{K^+}^+> = <Ra_{K^+} R^+> = (\Sigma V_K <a_{K^+}^+>) <a_{K^+}^+>/Q
\]

Thus

\[
Q = |\Sigma V_K <a_{K^+}^+>|
\]

(3.20)

The net result of this rotation is then

\[
H'_I = |\Sigma V_K <a_{K^+}^+> |(a_{o^+}^+ + a_{o^+}^{'}) + \Sigma n_{o^+} n_{o^{'}} -(E_o + \mu) \Sigma n_{o^{'}}
\]

(3.21)

\[
H'_S = \Sigma V_K <a_{o^+}^+> (a_{K^+}^+ + a_{K^+}^{'}) + \Sigma (e_{K^+} - \mu) n_{K^0}
\]

In this last equation we have replaced \( <a_{o^+}^+> \) by \( <a_{o^+}^{'},> \). This is legitimate since \( H'_I \) is real.
Indeed, spin symmetry is broken with the reservoir degeneracy consequence described in Section 1.3.

D. **Time Reversal Symmetry**

Time reversal symmetry is also broken because of the broken spin symmetry.
CHAPTER IV

MAGNETIC AND ELECTRIC PROPERTIES

Once the Hamiltonian of a system is known, one is left with the task of getting some useful information out of it. Those properties that are historically and experimentally significant to the problem under study are the responses to magnetic and electric fields. In what follows, a perturbation approach to the magnetic susceptibility and the electrical conductivity will be developed.

1. Magnetic Susceptibility

By definition the zero field magnetic susceptibility is

\[ \chi = \lim_{H \to 0^+} \frac{\partial M}{\partial H} \]

where \( M \) is the magnetization of the system

\( H \) is the magnetic field intensity

Since the general expression for \( M \) is:

\[ M = \epsilon(H) M_0 + HM_1 + \ldots \]

(4.2)

where \( \epsilon(H) = \begin{cases} +1 & H > 0 \\ 0 & H = 0 \\ -1 & H < 0 \end{cases} \)

\( M_0 = |\text{spontaneous magnetization}| \)

it is seen that both expressions for \( \chi \) lead to:
\[ \chi = \infty \text{ if } M_o \neq 0 \]  
\[ \chi = M_1 \text{ if } M_o = 0 \]  

(4.3)

This quantity then has to be calculated in the cluster approximation. Because of the limiting process \( H \to 0 \) appearing in the definition of \( \chi \), a numerical solution of the susceptibility is impractical whereas a perturbation approach to it is quite feasible. Unfortunately, this perturbation treatment is complicated by the presence of the electron reservoir which is, itself, also perturbed by the field. What follows is a generalization of the perturbation theory formalism to account for reservoir dependent Hamiltonians subjected to static, uniform magnetic fields.

A. **General Case**

Let us assume an unperturbed cluster Hamiltonian of the appropriate form:

\[ \mathcal{H}_{\text{cl}} = \mathcal{H}_0 + t \sum_l \langle \alpha_l^+ | (a^{+}_{\alpha_l} + a_{\alpha_l}^{-}) - \mu \sum_{i \sigma \nu} \Sigma n_{i \sigma} \rangle \]  

(4.4)

where \( t \) is a constant and \( \mathcal{H}_0 \) is the part of the cluster Hamiltonian, which is independent of the reservoir and the chemical potential. For our purposes, \( \mathcal{H}_0 \) is real and hermitian and thus, from Eq. (4.4), so is \( \mathcal{H}_{\text{cl}} \).

Under the perturbing influence of an external static, uniform magnetic field, parallel to the \( z \)-axis of the rotated cluster:

\[ \mathcal{H}'_{\text{cl}} = \mathcal{H}_0 + t \sum_l \langle \alpha_l^+ \rangle' | (a^{+}_{\alpha_l} + a_{\alpha_l}^{-}) \]  

\[ -\mu' \sum_{i \sigma \nu} n_{i \sigma} - \mu H \sum_{i \nu} (n_{i \nu} - n_{i \nu}^+) \]  

(4.5)
where \( \mu_0 \) is the magnetic moment of the electron and the primed values are perturbed ones.

Let us write the following first order expansions in powers of \( H (H \neq 0) \),

\[
|\langle a_+ \rangle'| = |\langle a_+ \rangle| - H|\langle a_+ \rangle|_\Delta
\]

(4.6)

\[
\mu' = \mu + H\mu_\Delta
\]

\[
\mathcal{H}' = \mu \sum_i \langle n_{i\uparrow} - n_{i\downarrow} \rangle' = \mu \sum_i \langle n_{i\uparrow} - n_{i\downarrow} \rangle + H \chi_i
\]

\[
n' = \sum_i \sum_\sigma \langle n_{i\sigma} \rangle' = \sum_i \sum_\sigma \langle n_{i\sigma} \rangle + Hn_\Delta
\]

where the suffix \( \Delta \) implies a perturbative incremental variation and the unprimed averages are calculated in the unperturbed representation of \( \mathcal{H}_{c\ell} \).

Using the well known perturbation series expansion of second quantization (10), the grand canonical partition function becomes

\[
p' = \text{Tr } e^{-\beta \mathcal{H}'_{c\ell}} = \text{Tr } e^{-\beta \mathcal{H}_{c\ell}} e^{\{1+H\beta \} \mathcal{H}_{c\ell}}
\]

(4.7)

\[
= \sum \mathcal{H}^{c\ell}_{c\ell}
\]

\[
x_0 \sum_\sigma \langle n_{i\sigma} \rangle + \mu \sum_i \chi_i + Hn_\Delta \sum_i \langle a_{i\downarrow}^+ (a_{i\downarrow} + a_{i\uparrow}) \rangle + \ldots
\]

with all higher order terms in \( H \) neglected. This is rewritten as
\[ p' = p(1 + H\langle\Delta p\rangle) \quad (4.8) \]

\[ \Delta p = \int_0^\beta \int d\tau e^{H_{cl}^\tau} \left[ u_0 \sum_i (n_{1+} - n_{1-}) + u_o \sum_{i\sigma} n_{i\sigma} ight. \\
+ t \sum_{\ell} \langle a_{\ell+}^+ a_{\ell+} \rangle e^{-H_{cl}^\tau} \left. \right] \\
+ t \sum_{\ell} \langle a_{\ell+}^+ a_{\ell+} \rangle e^{-H_{cl}^\tau} \]

It is then trivial to show that for any operator \( \Theta \),

\[ \langle \Theta \rangle' = \frac{T_R e^{-\beta H_{cl}^\prime}}{T_R e^{-\beta H_{cl}^\prime}} \langle \Theta \rangle + H \langle \Delta p(\Theta - \langle \Theta \rangle) \rangle \quad (4.9) \]

with all averages calculated in the unperturbed representation of \( H_{cl}^\prime \).

Therefore

\[ n_\Delta = \langle \Delta p \sum_{i\sigma} (n_{1\sigma} - n_{1\sigma}) \rangle \quad (4.10) \]

\[ x_1 = u_o \langle \Delta p \sum_{i} (n_{1+} - n_{1+}) + (n_{1+} - n_{1+}) \rangle \]

\[ |\langle a_{\ell+}^+ \rangle'| = |\langle a_{\ell+}^+ \rangle'| = |\langle a_{\ell+}^+ \rangle + H\langle a_{\ell+} - a_{\ell+} \rangle| \]

This last term needs rewriting in order to get \( \langle a_{\ell+}^+ \rangle \) out. Since \( H_{cl} \) as written in Eq. (4.1) is real, this automatically implies all averages are real. Thus
1. if $\langle a_{k^+} \rangle$ and $\langle \Delta p(a_{k^+} - a_{k^+}) \rangle > 0$

$$|\langle a_{k^+} \rangle + H\langle \Delta p(a_{k^+} - a_{k^+}) \rangle|$$

$$= |\langle a_{k^+} \rangle| + H\langle \Delta p(a_{k^+} - a_{k^+}) \rangle$$

and $\langle a_{k^+} \rangle_{\Delta} = -\langle \Delta p(a_{k^+} - a_{k^+}) \rangle$

2. if $\langle a_{k^+} \rangle$ and $\langle \Delta p(a_{k^+} - a_{k^+}) \rangle < 0$

$$|\langle a_{k^+} \rangle + H\langle \Delta p(a_{k^+} - a_{k^+}) \rangle|$$

$$= |\langle a_{k^+} \rangle| - H\langle \Delta p(a_{k^+} - a_{k^+}) \rangle$$

and $\langle a_{k^+} \rangle_{\Delta} = +\langle \Delta p(a_{k^+} - a_{k^+}) \rangle$

3. if $\langle a_{k^+} \rangle > 0$ and $\langle \Delta p(a_{k^+} - a_{k^+}) \rangle < 0$, and if $|H\langle \Delta p(a_{k^+} - a_{k^+}) \rangle| \leq |\langle a_{k^+} \rangle|$

$$|\langle a_{k^+} \rangle + H\langle \Delta p(a_{k^+} - a_{k^+}) \rangle|$$

$$= |\langle a_{k^+} \rangle| + H\langle \Delta p(a_{k^+} - a_{k^+}) \rangle$$

and $\langle a_{k^+} \rangle_{\Delta} = -\langle \Delta p(a_{k^+} - a_{k^+}) \rangle$
4. if \( <a_{\uparrow}^+> < 0 \) and \( <a_{\uparrow}^+ - a_{\uparrow}^+ > > 0 \) and if

\[
|H<\Delta p(a_{\uparrow}^+ - a_{\uparrow}^+)>| \leq |<a_{\uparrow}^+>|
\]

\[
|<a_{\uparrow}^+> + H<\Delta p(a_{\uparrow}^+ - a_{\uparrow}^+)>|
\]

\[
= |<a_{\uparrow}^+> - H<\Delta p(a_{\uparrow}^+ - a_{\uparrow}^+)>|
\]

and \( <a_{\uparrow}^+> \Delta = +<\Delta p(a_{\uparrow}^+ - a_{\uparrow}^+)>. \)

The condition, \( |H<\Delta p(a_{\uparrow}^+ - a_{\uparrow}^+)>| \leq |<a_{\uparrow}^+>| \), appearing in (3) and (4) will be satisfied in the limit \( H \rightarrow 0 \) except perhaps when \( <a_{\uparrow}^+> = 0 \). In this case,

\[
<\Delta p(a_{\uparrow}^+ - a_{\uparrow}^+)> = <\Delta p a_{\uparrow}^+> \text{ if } <a_{\uparrow}^+> = 0
\]

But then \( \mathcal{H}_{\text{cl}} = \mathcal{H}_{\text{o}} - \mu \sum_i \sigma_i n_i^\uparrow \) and \( \Delta p \) both conserve particles within the cluster since there is no longer any reservoir term. This means the eigenstates of the cluster are eigenstates of the number operator \( (n_{\text{cl}}) \).

Therefore

\[
<\Delta pa_{\uparrow}^+> = 0 \text{ if } <a_{\uparrow}^+> = 0
\]

since \( (\Delta pa_{\uparrow}^+) \) does not conserve particles within the cluster. Thus this condition \( |H<\Delta p(a_{\uparrow}^+ - a_{\uparrow}^+)>| \leq |<a_{\uparrow}^+>| \) is always satisfied.

This can best be summarized by:

\[
<a_{\uparrow}^+> \Delta = -\text{sign}(a_{\uparrow}^+) <\Delta p(a_{\uparrow}^+ - a_{\uparrow}^+)> \quad (4.11)
\]
But then, it is shown in Appendix E that the average number of electrons on any site of a spin inversion invariant Hamiltonian does not vary to first order in $H$, irrespective of whether or not this Hamiltonian conserves particles. Since the original Hamiltonian has such symmetry, the average electronic occupancy per site should remain constant. This condition must then be imposed on the cluster. The resulting requirement on $\mu\Delta$ is:

$$n_\Delta = \langle A p \sum_{i, \sigma} (n_{i\sigma} - \langle n_{i\sigma} \rangle) \rangle = 0$$

Substituting for $\Delta p$,

$$\mu_{\Delta} = \left\{ \nu_{\Delta} \int_{0}^{B} d\tau \langle e^{\sum_{i, \sigma} (n_{i\sigma} - n_{i\sigma}^{+})} \sum_{i, \sigma} (n_{i\sigma} - \langle n_{i\sigma} \rangle) \rangle \right\} / B$$

Substituting this expression for $\mu_{\Delta}$ into the expressions for $\langle a^{+}_{\Delta} \rangle$ and $X_{1}$, the following matrix equation results:

$$\begin{bmatrix}
A_{11} & 0 \\
A_{21} & 1
\end{bmatrix}
\begin{bmatrix}
\langle a^{+}_{\Delta} \rangle \\
X_{1}
\end{bmatrix}
= 
\begin{bmatrix}
B_{1} \\
B_{2}
\end{bmatrix}$$
\[ A_{11} = \left( 1 + \text{sign}(\langle a_{k^+} \rangle) \right) \left\{ t \int_0^\beta \Sigma (a_{k^+}^+ + a_{k^+}^-) e_{\ell_1} \right\} \ \mathcal{H}_{cl}^\top - \mathcal{H}_{cl}^\top \]

\[ \times (a_{k^+}^- - \langle a_{k^+} \rangle) \]

\[ - \int_0^\beta \Sigma (a_{k^+}^+ + a_{k^+}^-) e_{\ell_1} \Sigma (n_i^- - \langle n_i \rangle) \]

\[ x \int_0^\beta \Sigma (\Sigma n_{i\sigma} e_{i\sigma}) (a_{k^+}^- - \langle a_{k^+} \rangle)/B \]

\[ A_{21} = -\mu_0 \left\{ t \int_0^\beta \Sigma (a_{k^+}^+ + a_{k^+}^-) e_{\ell_1} \right\} \ \mathcal{H}_{cl}^\top - \mathcal{H}_{cl}^\top \]

\[ - \int_0^\beta \Sigma (a_{k^+}^+ + a_{k^+}^-) e_{\ell_1} \Sigma (n_i^- - \langle n_i \rangle) \]

\[ x \int_0^\beta \Sigma (\Sigma n_{i\sigma} e_{i\sigma}) (n_i^- - \langle n_i \rangle) \]

\[ \Sigma (n_i^- - \langle n_i \rangle)/B \} \]
\[ B_1 = -\text{sign}(\langle a_{z^+} \rangle) \{ \mu_0 \int_0^\beta d\tau < e \sum_{i} (n_{i^+} - n_{i^+})e_i (a_{z^+} - \langle a_{z^+} \rangle) \} \]

\[ - \mu_0 \int_0^\beta d\tau < e \sum_{i} (n_{i^+} - n_{i^+})e_i \sum_{i} (n_{i^+} - n_{i^+})e_i \]

\[ \times \int_0^\beta d\tau < e \sum_{i} n_{i^+} \sum_{i} (a_{z^+} - \langle a_{z^+} \rangle) / B \}

\[ B_2 = \mu_0 \int_0^\beta d\tau < e \sum_{i} (n_{i^+} - n_{i^+})e_i \sum_{i} (n_{i^+} - n_{i^+})e_i \]

\[ - \mu_0 \int_0^\beta d\tau < e \sum_{i} (n_{i^+} - n_{i^+})e_i \sum_{i} (n_{i^+} - n_{i^+})e_i \]

\[ \times \int_0^\beta d\tau < e \sum_{i} n_{i^+} \sum_{i} (a_{z^+} - \langle a_{z^+} \rangle) / B \]

All integrals of the type

\[ M = \int_0^\beta \mathcal{H} c_{l^+}^T - \mathcal{H} c_{l^+}^T \]

are evaluated in the following way
\[ M = \sum_{\gamma} \frac{e^{-\beta E_{\gamma}}}{E_{\gamma} - E_{a}} \frac{\langle a | A | \gamma \rangle \langle \gamma | C | a \rangle}{\text{Tr e} - \beta \mathcal{H}_{\text{cl}}} \]

with \[ \mathcal{H}_{\text{cl}} | a \rangle = E_{a} | a \rangle \]

Therefore

\[ X_{1} = -\frac{B_{1}A_{21}}{A_{11}} + B_{2} \quad (4.14) \]

and

\[ X = X_{1} \quad \text{if} \quad \Sigma_{i} <n_{1}^{+} - n_{1}^{-}> = 0 \quad (4.15) \]

\[ X = \infty \quad \text{if} \quad \Sigma_{i} <n_{1}^{+} - n_{1}^{-}> \neq 0 \]

B.) Special Case: Vanishing Reservoir

In the limiting case of a vanishing reservoir, \(<a_{+}> = 0\), the unperturbed cluster Hamiltonian recovers its lost spin symmetry. \(\mathcal{H}_{\text{cl}}\) then again conserves particles and this implies \(A_{21} = 0\). The consequence of spin rotational symmetry is

\[ \Sigma_{i} <n_{i}^{+} - n_{i}^{-}> = 0 \]

and as per Appendix E, \(X_{1}\) reduces to
\[ \chi_1 = B_2 = \mu_0^2 \int_0^\beta d\tau e^{\Sigma(n_{i^+} - n_{i^+})} \Sigma(n_{i^+} - n_{i^+})e^{\Sigma(n_{i^+} - n_{i^+})} \]  
\[ -i \chi_1 \]  
\[ \tag{4.16} \]

This is essentially the conventional result.*

2. **Electrical Conductivity**

By definition, the electrical conductivity \( \sigma \) is

\[ \sigma = \lim_{E \to 0} \frac{J}{E} \]

where \( J \) is the current and \( E \) the electric field. In order to calculate this parameter in the cluster approximation, a perturbation solution is favored, again because of the limiting process involved in calculating \( \sigma \).

The result of such an analysis is found in Kubo(11), Eq. (5.11), and the steady state, adiabatic, longitudinal electric conductivity is

\[ \sigma(\omega) = \lim_{\epsilon \to 0} \int_0^\beta d\lambda \int_0^\infty d\tau e^{-(i\omega+\epsilon)t} \langle J_x(-i\lambda)J_x(t) \rangle \]  
\[ \tag{4.17} \]

where again the thermodynamic averages are taken in the unperturbed Hamiltonian representation.

The above expression is derived for a lossless system, i.e., one without any joule losses. As shown in Appendix H, one way such losses can be introduced phenomenologically into the conductivity is by considering the \( \epsilon \) in Equation (4.17) not in the limit \( \epsilon \to 0 \), but as a loss parameter \( \epsilon > 0 \). The larger \( \epsilon \), the lossier the system. The reason we wish to consider a lossy

*See Kubo(11), Eq. 3.16.
system is that the D.C. conductivity for a lossless cluster is meaningless.
This point will be brought up later on.

A.) Properties

The integrals appearing in the expression for \( \sigma(\omega) \) can easily be performed in the representation of \( \mathcal{H}_0 \)

\[
\mathcal{H}_0 |\alpha> = E_a |\alpha>
\]

\[
p = \text{Tr e}^{-\mathcal{H}_0}
\]

and one gets for a lossy system

\[
\sigma(\omega) = \sum_{\alpha\gamma} \frac{(-\beta E_{\alpha} - \beta E_{\gamma}) |<\alpha | J_x |\gamma>|^2}{(E_{\gamma} - E_{\alpha}) p[i(\omega + E_a - E_{\gamma}) + \varepsilon]}
\]

(4.18)

Separating into real and imaginary parts

\[
R_e \sigma(\omega) = \sum_{\alpha\gamma} \frac{(-\beta E_{\alpha} - \beta E_{\gamma}) |<\alpha | J_x |\gamma>|^2 \varepsilon}{(E_{\gamma} - E_{\alpha}) p[(\omega + E_a - E_{\gamma})^2 + \varepsilon^2]}
\]

(4.19)

\[
I_m \sigma(\omega) = \sum_{\alpha\gamma} \frac{(-\beta E_{\alpha} - \beta E_{\gamma}) |<\alpha | J_x |\gamma>|^2 (\omega + E_a - E_{\gamma})}{(E_{\gamma} - E_{\alpha}) p[(\omega + E_a - E_{\gamma})^2 + \varepsilon^2]}
\]

We now catalogue some properties of the complex conductivity.
1. It is easily seen that $\sigma(\omega)$ is made up of a sum of resonant terms. These resonances occur at $\omega = E_\gamma - E_\alpha$, i.e., at excitation energies of the system, and $R e \sigma(\omega)$ is lorentzian shaped around each, with width $2\epsilon$ while $I m \sigma(\omega)$ has the usual reactive shape:

The width of $R e \sigma(\omega)$ being characteristic of the losses in the system, we are then justified in having characterized $\epsilon$ as the loss parameter.

2. It is easily verified that the following relation

\[ \frac{2}{\pi} \int_0^\infty R e \sigma(\omega) d\omega = -\lim_{\omega \to \infty} \omega I m \sigma(\omega) \]

(4.20)

holds.

3. In the high temperature region,

\[ \lim_{\beta \to 0} (e^{-E_\alpha} - e^{-E_\gamma}) = \beta(E_\gamma - E_\alpha) \]

and so
\[
\lim_{\beta \to 0} R_{x}(\omega) = \beta \pi \frac{|\langle \alpha | J_{x} | \gamma \rangle|^{2} \epsilon}{\alpha \gamma} \frac{p[(\omega+E_{\alpha} - E_{\gamma})^{2} + \epsilon^{2}]}{p[(\omega+E_{\alpha} - E_{\gamma})^{2} + \epsilon^{2}]}
\]

\[
\lim_{\beta \to 0} \frac{\delta E}{m} = -\beta \pi \frac{|\langle \alpha | J_{x} | \gamma \rangle|^{2} (\omega+E_{\alpha} - E_{\gamma})}{\alpha \gamma} \frac{p[(\omega+E_{\alpha} - E_{\gamma})^{2} + \epsilon^{2}]}{p[(\omega+E_{\alpha} - E_{\gamma})^{2} + \epsilon^{2}]}
\]

The electrical conductivity then decreases to zero like \( \beta \) at high temperature.

4. The lossless conductivity (\( \epsilon \to 0^{+} \)) in the limit of zero frequency can be deduced from Equation (4.19). It is

\[
\lim_{\omega \to 0} \lim_{\epsilon \to 0} R_{x}(\omega) = \frac{\pi \delta(E_{\alpha} - E_{\gamma})}{p} \frac{|\langle \alpha | J_{x} | \gamma \rangle|^{2}}{\alpha \gamma}
\]

\[
\lim_{\omega \to 0} \lim_{\epsilon \to 0} I_{x}(\omega) = \omega \frac{(\delta E_{\alpha} - \delta E_{\gamma})}{\alpha \gamma} \frac{|\langle \alpha | J_{x} | \gamma \rangle|^{2}}{p[\omega^{2} - (E_{\alpha} - E_{\gamma})^{2}]}
\]

This is the usual definition of the D.C. conductivity. However, this conductivity will be non-zero only if there are eigenstates of the system which are infinitely close in energy and which are coupled through the \( J_{x} \) operator. But in a cluster approximation, the cluster eigenstates are discrete and normally non-degenerate. It is then meaningless to talk of D.C. lossless conductivity in a cluster context since it would always be zero. What one must then do to investigate the conducting possibilities of a cluster is to try and excite electrons between eigenstates which might be coupled together by the current operator and then look at \( \sigma \). This can be
achieved by applying an alternating electric field or by introducing losses in the system which have the effect of scattering electrons between eigenstates of the system. As a matter of fact, in the limit of very large losses \((\varepsilon \to \infty)\) the low frequency limit of the conductivity in (4.19) is directly related to \(\sigma(\omega)\):

\[
\lim_{\varepsilon \to \infty} R e \sigma(\omega) = \frac{1}{\varepsilon} \frac{E}{\alpha \gamma} \frac{e^{-\beta E} - e^{-\beta E} \langle \alpha | J_\chi | \gamma \rangle^2}{p(E - E_\gamma)}
\]

\[
= \frac{1}{\varepsilon} \frac{2}{\pi} \int_0^\alpha R e \sigma(\omega) d\omega \tag{4.21}
\]

\[
\lim_{\varepsilon \to \infty} I m \sigma(\omega) = \frac{1}{\varepsilon} \frac{E}{\alpha \gamma} \frac{e^{-\beta E} - e^{-\beta E} \langle \alpha | J_\chi | \gamma \rangle^2}{p(E - E_\gamma)}
\]

In the lossy case \(I m \sigma(\omega) \ll R e \sigma(\omega)\) and one can essentially forget about the imaginary part of \(\sigma(\omega)\). For all practical purposes \(\sigma(\omega)\) is real (negligible phase angle).

Equation (4.21) tells us that the lossy conductivity is directly proportional to the integration of \(R e \sigma(\omega)\) over all frequencies. Thus one way to find out whether a cluster can possibly be made to conduct current at any frequency is by looking at the integrated conductivity or equivalently at the coefficient of the \(1/\varepsilon\) term in the lossy conductivity. If this forced conductivity remains zero, then the cluster is definitely an insulator.
B.) **Special Form**

We then choose to calculate this expression (4.21) for the conductivity. Making use of the expression for the current density operator in Appendix F:

\[ J_x = ie[x, H_0] = ie[\xi x \eta \chi \omega, H_0] \]

our useful expression for conductivity becomes

\[
\lim_{\epsilon \to 0} \sigma = \frac{2}{\epsilon} \sum_{\alpha, \gamma} (e^{-\beta E_{\alpha}} - e^{-\beta E_{\gamma}})(E_{\alpha} - E_{\gamma}) \frac{|\langle \alpha | \xi x \eta \chi \omega | \gamma \rangle|^2}{i \sigma} \tag{4.22}
\]
CHAPTER V

THE SOLUTION

PART A: HUBBARD'S HAMILTONIAN

1. Single Site Cluster

By far the simplest, easiest cluster solution is to a single-site cluster. One atom is pulled out of the system and coupled to the reservoir.

1.1 The general solution

The broken symmetry, single-site cluster Hamiltonian is, as per Equation (3.7):

$$\mathcal{H}_c = zT|a_+|^2 + |T(a_+^+a_+^+) + \ln n_+ - \mu(n_+^+n_+)$$

(5.1)

Here $z$ is the number of nearest neighbors ($= \frac{1}{6}$). The site quantum number $j$ has been dropped from the Hamiltonian since there is no ambiguity as to which site is involved. As will be recalled, the absolute value appearing in the reservoir term is a consequence of the special spin rotation leading to (3.7).

The unperturbed states of the cluster are

- $|0\rangle$ empty cluster
- $|\uparrow\rangle$ spin-up electron in the cluster
- $|\downarrow\rangle$ spin-down electron in the cluster
- $|\uparrow\downarrow\rangle$ filled cluster
The energy matrix $<\psi_a | \hat{H}_{cl} | \psi_b>$ is then

$$
\begin{array}{cccc}
|0> & |\uparrow> & |\downarrow> & |\uparrow \downarrow>
\end{array}
$$

$$
\begin{array}{cccc}
|0> & zT|<a_+>| & 0 & 0 \\
|\uparrow> & zT|<a_+>| & -\mu & 0 \\
|\downarrow> & 0 & -\mu & zT|<a_+>| \\
|\uparrow \downarrow> & 0 & 0 & zT|<a_+>| -2\mu + 1
\end{array}
$$

This matrix is easily diagonalized since it breaks up into two 2x2 submatrices. Although the ground state ($\beta = \infty$) was found analytically it becomes necessary to compute the eigenstates at non-zero temperatures because of the complexity of the self-consistency calculations. A three dimensional mesh for the variable $\mu$, $zT$, $\beta$ was set up. At each point, all the pertinent thermodynamic quantities were computed in the diagonalized representation. The self-consistency condition was inverted. Instead of requiring

$$
|<a_+>|_{\text{assumed}} = |<a_+>|_{\text{calculated}}
$$

at a given value of $zT$, the particular value of $zT$ satisfying the above condition for the given set of parameters $\mu$, $zT|<a_+|$, $\beta$ was calculated

$$
zT = \frac{(zT|<a_+|)_{\text{assumed}}}{|<a_+|_{\text{calculated}}}
$$
This was possible because $zT$ occurs only when paired with $|a_+>$ and so $zT|a_+>$ could be considered as the iteration variable.

The thermodynamic quantities that were calculated are:

\[
\langle a_+ \rangle = \frac{\text{Tr}(e^{-\beta \mathcal{H}} c_l a_+)}{\text{Tr} e^{-\beta \mathcal{H}} c_l}
\]

\[
n = \frac{\text{Tr} e^{-\beta \mathcal{H}} c_l (n_+ + n_-)}{\text{Tr} e^{-\beta \mathcal{H}} c_l}
\]

\[
M = \frac{\text{Tr} e^{-\beta \mathcal{H}} c_l (n_+ - n_-)}{\text{Tr} e^{-\beta \mathcal{H}} c_l}
\]

\[
x \quad \text{as per (4.14;15). All summations over the sites are reduced to the one site present. The parameter } t \text{ is equal to } zT.
\]

The electrical conductivity requires a bit of after-thought. The presence of an electrical field breaks up the translational invariance of the total system. The average thermodynamic behavior of the sites will then vary along the electrical field. The consequence is that it is no longer possible to study the whole system's behavior by looking only at a single one of its atoms. One must look at all the sites. In the cluster context, this would imply that one should look at each site and try to approximate the correlation between it and the rest of the system in a self-consistent way.
The best way this can be achieved in a somewhat unified way is by using the tensorial product concept introduced in Chapter II, Section 6. The whole system is represented by a tensorial product over all sites, each considered as a cluster. Thus the system can be thought of being formed by as many clusters as there are sites. The lack of translational invariance is then naturally accounted for without extra labor.

In a cluster approximation the states of the whole system become (see Section II.6):

$$|\alpha\rangle = \bigotimes_i |\alpha_i\rangle$$

that is a tensor product of the eigenstates of $\mathcal{H}_{c\mathbf{i}}$ on each site ($\mathcal{H}_{c\mathbf{i}} |\alpha_i\rangle = E_{\alpha_i} |\alpha_i\rangle$). As such, the partition function is

$$p = \bigotimes_i p_i = \bigotimes_i \text{Tr} e^{-\beta \mathcal{H}_{c\mathbf{i}}}$$

and the conductivity $\sigma$ would then be, using the thermodynamic equations (4.22):

* Since we are interested in the case $\epsilon \to \infty$ we need not worry about the effect of any perturbation of the reservoir and the chemical potential as was the case for the magnetic susceptibility in Section IV.1. The reason is that any such perturbations are proportional to $\epsilon^{-1}$ and as such can be forgotten in the thermodynamic average calculations. This effect would only enter to order $\epsilon^{-2}$ in the conductivity.
\[ \lim_{\varepsilon \to 0 \atop \omega \to 0} \sigma = \frac{e^2}{\varepsilon} \sum_{i} \langle \alpha_i \rangle \left( e^{\frac{\beta E}{\varepsilon}} - e^{-\frac{\beta E}{\varepsilon}} \right) \left( \sum_{\gamma} (E_{\alpha_i} - E_{\gamma}) \right) \left( \sum_{\sigma} \prod_{i} p_i \right) \]

\[ \times \left| \sum_{j} \left( \sum_{\sigma} \prod_{i} p_i \right) < \alpha_i | \Sigma \sum_{\gamma} (E_{\alpha_i} - E_{\gamma}) | \gamma_j > \right|^2 \]

After due simplification, this expression takes on the form:

\[ \sigma = \frac{e^2}{\varepsilon} \sum_{i} \langle \alpha_i \rangle \left( e^{\frac{\beta E}{\varepsilon}} - e^{-\frac{\beta E}{\varepsilon}} \right) \left( \sum_{\gamma} (E_{\alpha_i} - E_{\gamma}) \right) \left( \sum_{\sigma} \prod_{i} p_i \right) \]

\[ \times \left| < \alpha_i | n_i | \gamma_i > \right|^2 \]

Since all clusters are translationally invariant in the unperturbed case,

\[ \sigma = \frac{e^2}{\varepsilon} \left( \sum_{i} \langle \alpha_i \rangle \right) \left( e^{\frac{\beta E}{\varepsilon}} - e^{-\frac{\beta E}{\varepsilon}} \right) \left( \sum_{\gamma} (E_{\alpha_i} - E_{\gamma}) \right) \left( \sum_{\sigma} \prod_{i} p_i \right) \]

\[ \times \left| < \alpha | n | \gamma > \right|^2 \]

where now the \( |\alpha> \) states are cluster eigenstates. Therefore, to within a constant, we define the conductivity...
\[ \sigma^0 = \sum_{\alpha \gamma} \frac{(-\beta E')^\alpha (-\beta E')^\gamma (E^\gamma - E^\alpha) |\langle n| \gamma \rangle|^2}{p} \] (5.6)

This conductivity is then representative of the conductivity between sites or, in the cluster context, the conductivity between the reservoir and the cluster atom.

To perform the computations of all these quantities, double precision work was used mainly because of some critical terms in the expression for the susceptibility which involved subtraction of large numbers to yield a very small one. There was need of at least ten significant digits.

Computations were performed on a System/360 in the Fortran IV language.

Thereafter, any particular situation can be deduced by simple interpolation in this three-dimensional mesh.

1.2 Zero temperature analytic solution

At zero temperature, the self-consistent solution to the thermodynamic quantities of interest can be written down analytically. The algebra is tedious but elementary. We obtain:

a) \( 0 \leq n \leq 1 \)

For \( ZT \leq \frac{1}{2(2n-1)U_{-1}(2n-1)} \)

\[ |\langle a_+ \rangle|^2 = n(1-n) \]

\[ U_{-1}(x) = \begin{cases} 1 & x > 0 \\ 0 & x \leq 0 \end{cases} \]

\[ M = \begin{cases} \mu_n & n \neq 1 \\ 0 & n = 1 \end{cases} \]

\[ x = \infty \]

\[ \sigma^0 = 2zTn(1-n) \]
For \( zT \geq \frac{1}{2(2n-1)U_0(2n-1)} \)

\[ |\langle a_+ \rangle|^2 = \frac{1}{4} \left[ 1 - \left( \frac{I}{2zT} \right)^2 \right] \]

\[ M = \frac{(1-n_o)}{(1-n_o)n_o} \quad n_o = \frac{I-2zT}{4zT} \]

\[ X = \begin{cases} 
\infty & n \neq 1 \\
\frac{2\mu}{zT} \left( \frac{2zT/I+1}{2zT/I-1} \right)^n & n = 1 
\end{cases} \]

\[ \sigma^o = \frac{zT}{8} \left[ (2zT/I)^2 - 1 \right] \]

b) \( 1 \leq n \leq 2 \)

Replace \( n \) by \((2-n)\) everywhere in part a. This implies there is complete symmetry in the solution between holes and electrons.

1.3 Special case: Vanishing reservoir

If the reservoir vanishes, i.e., \( |\langle a_+ \rangle| = 0 \) the solution is trivial. It is the solution of a free atom. The unperturbed states of the atom are then diagonal.

\[ -\beta \mathcal{H} = \begin{pmatrix} \beta \mu & \beta(2\mu-I) \\ \beta(2\mu-I) & \beta \end{pmatrix} \]

\[ z = \text{Tr } e^{-\beta \mathcal{H}} = 1+2e^{+e} \]

\[ \langle n \rangle = 2(e^{\beta \mu}+e^{\beta(2\mu-I)})/z \]

\[ M = 0 \]

\[ X = 2\mu_0^{2} \beta e^{\beta \mu}/z \]

\[ \sigma^o = 0 \]
\[ \chi = \frac{\mu^2}{e} \frac{n}{kT[1 + \left(\frac{n-1}{2-n}\right) + \sqrt{(n-1)^2 + \frac{-\beta I}{n(2-n)}}]} \] (5.7)

2.2 Two-site cluster

The next step from the single-site cluster is obviously the two-site cluster. Although the specifics of the crystal structure are still suppressed, this cluster will nevertheless show a better dependence on the number of nearest neighbors than the single-site one. The larger size of the cluster should result in better correlation effects.

The cluster Hamiltonian is:

\[ \mathcal{H}_{cl} = -(z-1)T \left< a^+_1 \right| (a^+_1 + a^+_2 + a^+_1 + a^+_2) \] (5.8)

\[-T \Sigma \sigma \left( a^+_1 a^+_2 + a^+_2 a^+_1 \right) \]

\[ + I (n^+_1 n^+_1 + n^+_2 n^+_2) - \mu \Sigma \sigma (n^-_1 + n^-_2) \]

The reservoir has been assumed equal for both sites of the cluster. This excludes any Neel type ground states. The hopping integral T has been chosen negative as in the case of a normal upright band. The factor \((z-1)\) occurs because there are \((z-1)\) nearest neighbors to a cluster site which are outside of the cluster.
There are now 16 unperturbed cluster states.

| o;o > | cluster empty |
| t;o > | spin-up electron on site 1 |
| o; t> | spin-up electron on site 2 |
| t; o> | spin-down electron on site 1 |
| o; t> | spin-down electron on site 2 |
| t+; o> | site 1 filled |
| o; t+> | site 2 filled |
| t; t> | spin-up electrons on both sites |
| t+; t> | spin-down electrons on both sites |
| t+; t> | spin-up electron on site 1; spin-down on site 2 |
| t+; t> | spin down electron on site 1; spin-up on site 2 |
| t+; t> | site 1 filled; spin-up electron on site 2 |
| t+; t> | site 1 filled; spin-down electron on site 2 |
| t+; t> | site 2 filled; spin-up electron on site 1 |
| t+; t> | site 2 filled; spin-down electron on site 1 |
| t+; t> | cluster filled |

However, the energy matrix can be factored more easily in the following representation:
\[ \phi_0 = |0;0> \]
\[ \phi_{11} = \frac{1}{\sqrt{2}} (|+;0 + |0;+>) \]
\[ \phi_{12} = \frac{1}{\sqrt{2}} (|+;0> - |0;+>) \]
\[ \phi_{13} = \frac{1}{\sqrt{2}} (|+;0> + |0;+>) \]
\[ \phi_{14} = \frac{1}{\sqrt{2}} (|+;0> - |0;+>) \]
\[ \phi_{21} = |+;+> \]
\[ \phi_{22} = |+;+> \]
\[ \phi_{23} = \frac{1}{2} (|+;0> - |+;+> + |+;+> + |0;++>) \]
\[ \phi_{24} = \frac{1}{2} (|+;0> + |+;+> - |+;+> + |0;++>) \]
\[ \phi_{25} = \frac{1}{2} (|+;0> + |+;+> + |+;+> - |0;++>) \]
\[ \phi_{26} = \frac{1}{2} (|+;0> - |+;+> - |+;+> - |0;++>) \]
\[ \phi_{31} = \frac{1}{\sqrt{2}} (|+;+++ |+;++>) \]
\[ \phi_{32} = \frac{1}{\sqrt{2}} (|+;++- |+;++>) \]
\[ \phi_{33} = \frac{1}{\sqrt{2}} (|+;+++ |;++>) \]
\[ \phi_{34} = \frac{1}{\sqrt{2}} (|+;++- |;++>) \]
\[ \phi_4 = |++;++> \]
The energy submatrices are

\[
\begin{align*}
\phi_0 & = \begin{bmatrix} \phi_{01} & \phi_{11} \\ 0 & -R \end{bmatrix} & \phi_{11} & = \begin{bmatrix} \phi_{12} & \phi_{21} \\ -u+T & R \end{bmatrix} \\
\phi_{11} & = \begin{bmatrix} -R & -u-T \end{bmatrix} & \phi_{21} & = \begin{bmatrix} R & -2\mu \end{bmatrix}
\end{align*}
\]

\[
\begin{align*}
\phi_{22} & = \begin{bmatrix} \phi_{22} & \phi_{34} \\ -2\mu & -R \end{bmatrix} & \phi_{34} & = \begin{bmatrix} \phi_{33} & \phi_4 \\ -3\mu+T+I & -R \end{bmatrix} \\
\phi_{34} & = \begin{bmatrix} -R & -3\mu-T+I \end{bmatrix} & \phi_4 & = \begin{bmatrix} -R & -4\mu+2I \end{bmatrix}
\end{align*}
\]

\[
\begin{align*}
\phi_{13} & = \begin{bmatrix} \phi_{13} & \phi_{24} \\ -u-T & -R \end{bmatrix} & \phi_{24} & = \begin{bmatrix} \phi_{23} & \phi_{31} \\ -R & -2\mu-2T+I/2 \end{bmatrix} \\
\phi_{23} & = \begin{bmatrix} 0 & I/2 \end{bmatrix} & \phi_{31} & = \begin{bmatrix} 0 & -2\mu+2T+I/2 \end{bmatrix}
\end{align*}
\]

\[
\begin{align*}
\phi_{31} & = \begin{bmatrix} 0 & 0 \end{bmatrix} & \phi_{31} & = \begin{bmatrix} -R & -3\mu+T+I \end{bmatrix}
\end{align*}
\]
\[
\begin{pmatrix}
\phi_{14} & \phi_{26} & \phi_{25} & \phi_{32} \\
-\mu + T & -R & 0 & 0 \\
-\mu & -2\mu + I/2 & I/2 & 0 \\
0 & I/2 & -2\mu + I/2 & -R \\
0 & 0 & -R & -3\mu - T + I
\end{pmatrix}
\]

with \( R = \sqrt{2(z-1)}T|<a_+>| \)

The 2x2 matrices are easily diagonalized, but such is not the case for the 4x4 ones. The need for a computerized solution is obvious. The usual diagonalization technique would involve the use of a diagonalizing program using the Jacobi pivot method. However the double precision requirement favored an exact solution. This was done by solving the fourth degree secular equation. Once the eigenvalues were found, the eigenvectors followed easily. The fourth degree equations were solved by the Lagrange method \(^{(12)}\) with a trigonometric solution to the auxiliary third degree equation.

The problem was set up on a four-dimensional mesh with the variables \( \mu, R, T, \beta \). The fourth dimension \( T \) was required since \( T \) is no longer solely associated with the reservoir. At each point, the pertinent thermodynamic values were calculated. The self-consistency was satisfied by comparing the value of \( T \) used at given \( \mu, R, \beta \), with the calculated one
and then by interpolating all data back to this correct value.

The thermodynamic averages calculated were:

\[ T_{\text{calculated}} = \frac{((z-1)T|\langle a_+ \rangle|)_{\text{assumed}}}{(z-1)|\langle a_+ \rangle|_{\text{calculated}}} \]

\[ <a_+ > = \frac{\text{Tr}(e^{-\beta \mathcal{H}_{c\mathcal{I}} a_{1_1}})}{\text{Tr} e^{-\beta \mathcal{H}_{c\mathcal{I}}}} \]

\[ n = \frac{\text{Tr} e^{-\beta \mathcal{H}_{c\mathcal{I}} (n_{1_1} + n_{1_1})}}{\text{Tr} e^{-\beta \mathcal{H}_{c\mathcal{I}}}} \]

\[ M = \frac{\text{Tr} e^{-\beta \mathcal{H}_{c\mathcal{I}} (n_{1_1} - n_{1_1})}}{\text{Tr} e^{-\beta \mathcal{H}_{c\mathcal{I}}}} \]

\[ \chi \quad \text{as per (4.14;15). The site summations extend over the two cluster site. The parameter t was equal to } -(z-1)T. \]

There are now two contributions to the conductivity. This can be seen by using the tensor product state concept derived for the single-site cluster. Using Eq. (5.3) and the concept of all clusters being lined up parallel to the electric field, one gets
\[
\lim_{\varepsilon \to 0} \omega \rightarrow 0 \quad \sigma = \frac{2}{\varepsilon} \sum_{m} \left( \frac{x_{m_1} + x_{m_2}}{2} \right)^2 \sum_{(\gamma) m} \frac{-\beta E_{\alpha_m} - \beta E_{\gamma_m}}{(e^{\frac{\alpha_m - e \gamma_m}{\varepsilon}} - 1) (E_{\alpha_m} - E_{\gamma_m})}
\]

\[
\left| <\alpha_m | n_{m_1} + n_{m_2} | \gamma_m > \right|^2
\]

\[
+ \frac{2}{\varepsilon} \sum_{m} \left( \frac{x_{m_1} - x_{m_2}}{2} \right)^2 \sum_{(\gamma) m} \frac{-\beta E_{\alpha_m} - \beta E_{\gamma_m}}{(e^{\frac{\alpha_m - e \gamma_m}{\varepsilon}} - 1) (E_{\alpha_m} - E_{\gamma_m})}
\]

\[
\left| <\alpha_m | n_{m_1} - n_{m_2} | \gamma_m > \right|^2
\]

\[
+ \frac{2}{\varepsilon} \sum_{m} \left( \frac{x_{m_1} + x_{m_2}}{2} \right) \left( \frac{x_{m_1} - x_{m_2}}{2} \right) \sum_{(\gamma) m} \frac{-\beta E_{\alpha_m} - \beta E_{\gamma_m}}{(e^{\frac{\alpha_m - e \gamma_m}{\varepsilon}} - 1) (E_{\alpha_m} - E_{\gamma_m})}
\]

\[
x (E_{\alpha_m} - E_{\gamma_m}) <\alpha_m | n_{m_1} + n_{m_2} | \gamma_m > <\gamma_m | n_{m_1} - n_{m_2} | \alpha_m >
\]

where the summation "m" is over all clusters.

Again using the translational invariance of all clusters in the ensemble* and the fact \( \Sigma (x_{m_1} + x_{m_2})(x_{m_1} - x_{m_2}) = 0, \)

*Remember, the averages are calculated in the unperturbed representation where the system is translationally invariant.
\[ \sigma = \frac{e^2}{c} \left[ \frac{1}{m} \left( \frac{x_{m_1} + x_{m_2}}{2} \right)^2 \right] \sum_{\alpha \gamma} \left( \frac{e^{\beta E_\alpha} - e^{\beta E_\gamma}}{p} \right) \]

\[ \times |\langle \alpha | n_1 + n_2 | \gamma \rangle|^2 \]

\[ + \frac{e^2}{c} \left[ \frac{1}{m} \left( \frac{x_{m_1} - x_{m_2}}{2} \right)^2 \right] \sum_{\alpha \gamma} \left( \frac{e^{\beta E_\alpha} - e^{\beta E_\gamma}}{p} \right) (E_\gamma - E_\alpha) \]

\[ \times |\langle \alpha | n_1 - n_2 | \gamma \rangle|^2 \]

where now \(|\alpha\rangle, |\gamma\rangle\) are eigenstates of the cluster. One sees that this conductivity can be subdivided into two parts. The first term of (5.10) depends directly on the reservoir. If the reservoir were zero then so would this term. Since the reservoir is coupled only to the cluster sites on the periphery of the cluster (nearest neighbor hopping only) it turns out that only these sites contribute to the first term. For this reason this part of the expression for the conductivity will be labelled peripheral conductivity. To within a constant, it is

\[ \sigma_p = \sum_{\alpha \gamma} \left( \frac{e^{\beta E_\alpha} - e^{\beta E_\gamma}}{p} \right) (E_\gamma - E_\alpha) |\langle \alpha | n_1 + n_2 | \gamma \rangle|^2 \]  

(5.11)

*This aspect will be further commented on in Section VI.5.*
The second part of (5.10) exists whether the reservoir is zero or not. This term will be recognized to be, within a constant, the conductivity of the atoms within the cluster. It is the intrinsic part of the conductivity. It will be labelled bulk conductivity and it is within a constant:

$$\sigma_B = \sum_{\gamma} \frac{\beta E - \beta E_a}{\gamma_p} (E - E_a) |<a|n_1 - n_2 |\gamma>|^2$$  \hspace{1cm} (5.12)$$

Again to order $\epsilon^{-1}$, the perturbation of the reservoir and the chemical potential are negligible as for the single-site cluster.

PART B: ANDERSON'S HAMILTONIAN

The Anderson problem is basically a single-site cluster with a more involved self-consistency condition. It will now be shown that the impurity part of the Hamiltonian is essentially equivalent to the single-site cluster approximation to Hubbard's Hamiltonian.

The two separated sub-Hamiltonians as derived in (3.21) are:

$$\hat{H} = \sum_{\sigma} n_{\sigma}^+ n_{\sigma} - (E_0 + \mu) \sum_{\sigma} n_{\sigma}$$  \hspace{1cm} (5.13)$$

$$+ \sum_{\sigma} \sum_{\nu} (E_{\nu} - E_a) |<a_{\sigma}^+ |a_{\nu}^{-}\rangle|$$

$$\hat{H}_S = \sum_{\sigma} \sum_{\nu} \sum_{\nu} (E_{\nu} - E_a) |<a_{\sigma}^+ |a_{\nu}^{-}\rangle|$$

Unfortunately $\hat{H}_S$ is still a many-body Hamiltonian involving all electrons with their anticommutation rules. The exact solution to $\hat{H}_S$
would be involved, but a lot of information can be obtained with a minimal amount of work. It is possible to effectively isolate the dependence of the impurity on the s-band. This will now be attempted.

The equation of motion method(13) will be used to derive the needed information. We shall now define the time ordered functions used in what follows:

a) single-operator function

\[
\langle a_{k\sigma}(t) \rangle = \langle a_{k\sigma} \rangle = \frac{\text{Tr} e^{-\beta \mathcal{H}} a_{k\sigma} e^{-\beta \mathcal{H}}}{\text{Tr} e^{-\beta \mathcal{H}}}
\]

Note this function is time independent. The cyclic property of the trace kills the single-time dependence.

b) two-operator function

\[
\langle a_{k\sigma}(t) ; a_{k'\sigma'}(t') \rangle = \frac{\text{Tr} e^{-\beta \mathcal{H}} \text{T} a_{k\sigma}(t) a_{k'\sigma'}(t') e^{-\beta \mathcal{H}}}{\text{Tr} e^{-\beta \mathcal{H}}}
\]

where T = Wick's time ordering operator.

c) three-operator function

\[
\langle a_{k\sigma}(t) a_{k''\sigma''}(t) ; a_{k'\sigma'}(t') \rangle = \frac{\text{Tr} e^{-\beta \mathcal{H}} \text{T} a_{k\sigma}(t) a_{k''\sigma''}(t) a_{k'\sigma'}(t') e^{-\beta \mathcal{H}}}{\text{Tr} e^{-\beta \mathcal{H}}}
\]
All of the above definitions are also applicable to creation as well as destruction operators. These unconventional functions occur because of the non-conservation of electrons in the uncoupled s-band.

Let us now look at the equation of motion of \( <a_{k'0}^+> \). For this we shall need to know that

\[
\frac{\partial}{\partial t} \Theta(t) = [\Theta(t), \mathcal{H}(t)]
\]

and

\[
[a_{k\sigma}, a_{k'\sigma'}^+] = 2a_{k\sigma} a_{k'\sigma'}
\]

\[
[a_{k\sigma}, a_{k'\sigma'}^+] = -\delta_{(k-k')} \delta_{\sigma\sigma'} + 2a_{k\sigma} a_{k'\sigma'}^+
\]

Then

\[
(i \frac{\partial}{\partial t} + \mu - \varepsilon_k) <a_{k\tau}^+>(t) = -V_k <a_{0\tau}^+>
\]

\[\begin{align*}
+ 2 \sum V_{k''} <a_{0\tau}^+><a_{k\tau}^+>(t) a_{k''\tau'}^+(t) \\
+ 2 \sum V_{k''} <a_{0\tau}^+><a_{k\tau}^+>(t) a_{k''\tau'}^+(t)
\end{align*}\]

On the other hand

\[
(i \frac{\partial}{\partial t} + \varepsilon_{k''} - \varepsilon_k) <a_{k\tau}^+>(t) a_{k''\tau'}^+(t) = V_{k''} <a_{0\tau}^+><a_{k\tau}^+>(t)
\]

\[\begin{align*}
- V_k <a_{0\tau}^+><a_{k\tau}^+>(t)
\end{align*}\]

\[
(i \frac{\partial}{\partial t} + 2\mu - \varepsilon_k - \varepsilon_{k''}) <a_{k\tau}^+>(t) a_{k''\tau'}^+(t) = V_k <a_{0\tau}^+><a_{k\tau}^+>(t)
\]

\[\begin{align*}
- V_k <a_{0\tau}^+><a_{k\tau}^+>(t)
\end{align*}\]
Since all these single time averages are really time independent,

\[ \langle a_{K^+} \rangle = -\frac{V_{K^+} a_{o^+}}{(\mu - \varepsilon_K)} + 2 \sum_{K''} \frac{V_{K''} \langle a_{o^+} \rangle^2 [V_{K''} \langle a_{K^+} \rangle - V_{K''} \langle a_{K''} \rangle]}{(\mu - \varepsilon_K)(\varepsilon_{K''} - \varepsilon_K)} \]  
(5.14)

\[ + 2 \sum_{K''} \frac{V_{K''} \langle a_{o^+} \rangle^2 [V_{K''} \langle a_{K^+} \rangle - V_{K''} \langle a_{K''} \rangle]}{(\mu - \varepsilon_K)(2\mu - \varepsilon_K - \varepsilon_{K''})} \]

From this last equation, \( \langle a_{K^+} \rangle \) is seen to have a pole at the chemical potential level, i.e., when \( \varepsilon_K = \mu \). Since \( V_K \) is of order \( N^{-1/2} \) it can be inferred that as \( N \to \infty \), \( \langle a_{K^+} \rangle \) exists only at its pole, i.e., at the chemical potential. Hopping into the s–band can only occur at the chemical potential.

Let us now calculate the reservoir term \( |\Sigma V_K \langle a_{K^+} \rangle| \). Going over to the continuum for the s–band

\[ \varepsilon \Rightarrow N \int dE \rho(E) ; \varepsilon_K \Rightarrow E \]

where \( \rho(E) \) is the density of states of the unperturbed s–band, we get
\[ T V \kappa \left\{ a^*_\kappa \right\} = -N \int \frac{dE}{dE'} \frac{\rho(E)\left\langle V^2\kappa \right\rangle_{E,E_0}^E \left\langle a^*_\kappa \right\rangle_{E,E_0}^E}{(u-E)(u-E')} \]
\[ + 2N^2 \int dE' \rho(E) \rho(E') \left\langle \left\langle V^2\kappa \right\rangle_{E,E_0}^E \left\langle a^*_\kappa \right\rangle_{E,E_0}^E \right\rangle' \]
\[ - \frac{\left\langle V^2\kappa \right\rangle_{E,E} \left\langle a^*_\kappa \right\rangle_{E,E}^E}{(u-E)(u-E')} \]
\[ + 2N^2 \int dE' \rho(E) \rho(E') \left\langle \left\langle V^2\kappa \right\rangle_{E,E_0}^E \left\langle a^*_\kappa \right\rangle_{E,E_0}^E \right\rangle_{(2u-E)} \]
\[ - \frac{\left\langle V^2\kappa \right\rangle_{E,E} \left\langle a^*_\kappa \right\rangle_{E,E}^E}{(u-E)(2u-E')} \]

The averages \( \langle \ldots \rangle_E \) indicate an appropriate average over a constant energy surface \( E \).

The best way to evaluate these integrals is via the complex plane.

In order to do this, the mathematical expression for \( \rho(E) \), normally confined on the real axis between its zeros, will be analytically continued to the whole complex plane. At the zeros \( E_0 \) of \( \rho(E) \), it will now be shown that \( \rho(E) \) has a branch point of the form

\[ \rho(E) \propto (E-E_0)^{1/2} \]

At the bottom or top of a band, the energy normally goes as \( (E-E_0) = k^2 \).

This means the summation
\[ \frac{1}{\mathcal{K}} \Rightarrow \frac{N}{(2\pi)^3} \int d\mathcal{K} = N \int dE \rho(E) \]

becomes, at those critical points

\[ \frac{N}{(2\pi)^2} \int dkk^2 = N \int dE (E - E_0)^{1/2} \]

This dictates the behavior of \( \rho(E) \) at the critical points to be

\[ \rho(E) = (E - E_0)^{1/2} \]

Q.E.D.

The branch cut is chosen to be between the branch points. The integration path then circles the branch cut as shown below:

![Diagram showing the branch cut and integration path]

Whatever poles of the integrands lie on the branch cut, they are simply displaced infinitesimally from the cut. Since \( \rho(E) \) has a zero at the branch points, the contribution to the integral from the small circles around them is zero. The only effect those branch points have is to add a phase factor \( e^{i\pi} \) each time around them. Setting the phase to be zero at point 0, \( (e^{10} = 1) \), the path integral is then
\[ \Phi \, d\rho(E)F(E) = e^{\frac{3\pi}{2}} \int_1^2 d\rho(E)F(E) \]

\[ + e^{\frac{\pi}{2}} \int_3^4 d\rho(E)F(E) \]

\[ = -2\pi i \int_1^2 d\rho(E)F(E) \]

The calculus of residues tells

\[ \Phi \, d\rho(E)F(E) = -2\pi i \sum \text{residues} \]

Since \( \rho(E) \) is analytic on the branch cut, then

\[ \Phi \, d\rho(E)F(E) = \pi \sum \text{residues} \]

From this it is obvious that of the terms appearing on the right of the expression for \( \Sigma V_{a_{\bar{K}^+}} \), only the first one will remain, the other two cancelling one another:

\[ \Sigma V_{a_{\bar{K}^+}} = N\pi \rho(\mu)\langle V_{\bar{K}^+}^2 \rangle \langle a_{\bar{K}^+} \rangle \]

As did Anderson, we define a width parameter

\[ \Delta = \pi \rho(\mu)\langle NV_{\bar{K}^+}^2 \rangle \mu \]  

and so

\[ \Sigma V_{a_{\bar{K}^+}} = \Delta \langle a_{\bar{K}^+} \rangle \]  

(5.15a)

(5.15b)
Finally, in order to get some insight concerning the chemical potential, let us look at the following equation of motion

\[
\left( i \frac{3}{\hbar} + \mu - \epsilon_K \right) \langle a_{K_0}^{\dagger} (t); a_{K^0}^+ (t') \rangle = i \delta(t-t')
\]

\[
- V_K \langle a_{o^+}^+ \rangle \langle a_{K^+}^+ (t); a_{K^+}^+ (t') \rangle + 2 \Sigma V_{K''} \langle a_{o^+}^+ \rangle \langle a_{K^+}^+ (t); a_{K^+}^+ (t') \rangle
\]

\[
+ 2 \Sigma V_{K''} \langle a_{o^+}^+ \rangle \langle a_{K^+}^+ (t); a_{K^+}^+ (t') \rangle
\]

But then

\[
\left( i \frac{3}{\hbar} + \epsilon_K - \epsilon_{K''} \right) \langle a_{K_0}^+ (t); a_{K''}^+ (t') \rangle = -i \delta(t-t') \langle a_{K''}^+ (t') \rangle
\]

\[
- V_K \langle a_{o^+}^+ \rangle \langle a_{K''}^+ (t); a_{K''}^+ (t') \rangle \delta_{o^+}
\]

\[
+ V_{K''} \langle a_{o^+}^+ \rangle \langle a_{K''}^+ (t); a_{K''}^+ (t') \rangle
\]

\[
\left( i \frac{3}{\hbar} + 2 \mu - \epsilon_K - \epsilon_{K''} \right) \langle a_{K_0}^+ (t); a_{K''}^+ (t') \rangle = \]

\[
= i \delta(t-t') \left[ \delta(K-K'') \delta_{o^+} \langle a_{K''}^+ \rangle - \langle a_{K''}^+ \rangle \right]
\]

\[
- V_K \langle a_{o^+}^+ \rangle \langle a_{K''}^+ (t); a_{K''}^+ (t') \rangle \delta_{o^+} + V_{K''} \langle a_{o^+}^+ \rangle \langle a_{K''}^+ (t); a_{K''}^+ (t') \rangle
\]
Transforming to Fourier series

\[-1 \frac{\pi v}{\tau} (t-t')\]

\[
\langle 0(t-t') \rangle = \frac{1}{\tau} \sum_{v} e^{2\pi i v} \langle \Theta \mid \psi \rangle,
\]

\[
(\frac{\pi v}{\tau} + \mu - \varepsilon_{k}) \langle a_{k}^{+} a_{k} \mid \psi \rangle = i V_{k} a_{0}^{+} \langle a_{k}^{+} + \delta \mid \psi \rangle \delta
\]

\[
+ 2 \sum_{k''} \frac{V_{k''} a_{0}^{+}}{(\pi v/\tau + \varepsilon_{k''} - \varepsilon_{k})} [-i a_{k''}^{+} - V_{k'} a_{0}^{+} \langle a_{k}^{+} + \delta \mid \psi \rangle a_{k''}^{+} + V_{k'} a_{0}^{+} \langle a_{k}^{+} + \delta \mid \psi \rangle]
\]

\[
+ V_{k'} a_{0}^{+} \langle a_{k}^{+} + \delta \mid \psi \rangle
\]

\[(5.16)\]

Dropping all terms of order \( N^{-1/2} \) or higher,

\[
(\frac{\pi v}{\tau} + \mu - \varepsilon_{k}) \langle a_{k}^{+} a_{k} \mid \psi \rangle \simeq i
\]

\[
+ 2 \sum_{k''} \frac{V_{k''} a_{0}^{+}}{(\pi v/\tau + \varepsilon_{k''} - \varepsilon_{k})} [-i a_{k''}^{+} - V_{k'} a_{0}^{+} \langle a_{k}^{+} + \delta \mid \psi \rangle a_{k''}^{+} + V_{k'} a_{0}^{+} \langle a_{k}^{+} + \delta \mid \psi \rangle]
\]

\[
+ V_{k'} a_{0}^{+} \langle a_{k}^{+} + \delta \mid \psi \rangle
\]
From Anderson's work, it is to be expected that the poles of this function should be unaltered from the unperturbed case. It would then seem wise to look for solutions of the form

\[
\frac{\pi \nu}{\tau} = \epsilon_k^{-\mu + \Theta(N^{-1/2})}
\]

Substituting this value in the right side of this last equation,

\[
(\frac{\pi \nu}{\tau} + \mu - \epsilon_k) \langle a_{k_0}^+ a_{k_0}^+ | v \rangle = 1
\]

\[
+ 2 \sum_{k''} \left[ \frac{V_{k''} \langle a_{0+}^+ a_{k_0}^+ | v \rangle - i V_{k''} \langle a_{0+} a_{k_0}^+ | v \rangle}{(\epsilon_k - \mu)} \right]

\]

\[
+ 2 \sum_{k''} \left[ \frac{V_{k''} \langle a_{0+}^+ a_{k_0}^+ | v \rangle - i V_{k''} \langle a_{0+} a_{k_0}^+ | v \rangle}{(\mu - \epsilon_k'' \Theta(N^{-1/2})}

\]

It has just been verified that the poles of this function remain unperturbed to order \(N^{-1/2}\). This implies the s-band density of states remains the same to order \(N^{-1/2}\) and the same must then be true for the chemical potential. It is controlled exclusively by the s-band because it holds the great majority of electrons.

The following conclusions emerge from this analysis:
a) The hopping between the impurity and the s-band can only occur at the chemical potential within the band. The chemical potential is essentially unperturbed.

b) The s-band controls the chemical potential.

c) The width parameter $\Delta$ is the controlling parameter in the impurity problem.

These conclusions were also deduced by Anderson\textsuperscript{(9)} and Schrieffer\textsuperscript{(14)} et al. in the course of their analysis.

The problem is now very simplified, at least for the impurity. The chemical potential can be arbitrarily set to zero and thus:

$$H_I = \ln o^+ e^{-E_o} \sum_o + \Delta |a_o^+\rangle \langle a_o^+ + a_o^+|$$  \hspace{1cm} (5.17)

Comparing this impurity Hamiltonian with the single-site cluster one for Hubbard's Hamiltonian in (5.1) it is enlightening to see the two have identical form with

$E_o$ substituted for $\mu$

$\Delta$ substituted for $zT$.

The solution to Hubbard's single-site cluster can then be carried over to the impurity. The s-band solution would imply solving (5.14)(5.16). This proved to be too much of a task with the presently available computer facilities.
CHAPTER VI

THE RESULTS

PART A: HUBBARD'S HAMILTONIAN IN THE SINGLE-SITE CLUSTER APPROXIMATION

1. $\beta = \infty$ Electrical Properties

1.1 Conductivity singularity

Figure (6.2) shows the $\beta = \infty$ dependence of the hopping per electron on the half-bandwidth ratio $ZT/I$. The striking characteristic of these curves is the presence of singular points on those curves with an occupancy per site between .5 and 1.5 electrons. At these points there is a discontinuity in the slope. This same property is reflected in the conductivity of Figure (6.3). Past a critical half-bandwidth ratio $(ZT/I)_c$ the conductivity suddenly increases. The locus of this critical point is shown in Figure (6.4).

1.2 Insulator-conductor transition

Consider the half-filled band case $n = 1$. For $ZT/I << .5$, the conductivity is zero and the solid is an insulator. But as soon as $ZT/I > .5$, the conductivity increases rapidly. This could then be classified as an insulator-conductor transition. This effect was first postulated by Mott (15). He reasoned that when the atoms of a solid are far apart, the tendency to hop is very small. Since each atom has one electron, hopping could only be achieved at the expense of a doubly occupied atom. This is energetically unfavorable because of the strong Coulomb repulsion. This effect would favor an insulator state devoid of hopping. As the atoms are brought closer together, the electronic overlap between atoms gets bigger,

* These $\beta=\infty$ properties have been deduced analytically in Section V.1.
i.e., $T$ gets larger. It might be expected that at a critical interatomic
distance the lowering of energy from the hopping would be sufficient to
compensate for the increase in Coulomb energy resulting from the formation
of doubly occupied atoms. The conductor state would be favored from then
on. This would result in an insulator-conductor transition. Mott pre-
dicted a discontinuous jump in the conductivity. This is not observed here
although the transition is rapid enough that such a jump might be expected
of a very large cluster. However, Mott might be wrong for this model.

The transition point was calculated by Hubbard\(^{(7)}\) to be at $ZT/I = 0.577$
while the work of Kemeny\(^{(6)}\) shows it to occur at $ZT/I = 0.63$ for the simple-
cubic structure. This prediction from the single-site cluster theory is
then comparable to those of the above mentioned authors. This is gratifying
considering the simplicity of the model used.

1.3 Conductor-conductor transition

The presence of a transition at values of $0.5 \leq n \neq 1 \leq 1.5$ comes
somewhat as a pleasant surprise. To our knowledge, this effect had not
been hinted in the works of Mott, Hubbard and Kemeny. The increase in
conductivity is then reminiscent of a conductor-conductor transition.

This again makes physical sense in the light of the previous arguments
on the Mott transition. For $n < 1$, when the atoms of the solid are far
apart, there would be some hopping onto the unoccupied atoms whereas the
occupied ones would be avoided because of the Coulomb repulsion. The solid

*The same arguments can be carried out for $n > 1$ by considering holes instead of electrons.
would then show some conductivity, increasing with the number of unoccupied sites available to electron hopping. This is observed. The conductivity at a given ZT/I increases with decreasing n, i.e., with increasing number of empty sites. Moreover the fact that the hopping is constant in the small ZT/I region, implies the hopping onto unoccupied sites is independent of ZT. This should be so since this hopping would be expected to be maximized regardless of ZT in order to attain a minimum in hopping energy. The number of unoccupied sites remaining constant with ZT, so would this maximized hopping.

As the atoms draw closer together, there should again be a critical interatomic distance at which the lowering of energy in hopping onto occupied sites would overcome the increase in Coulomb energy. The conductivity would then increase because of the added hopping freedom. The larger ZT, the more these ionic states would be favored and the larger the conductivity would get. This is observed. Now, as the number of electrons decreases, the number of occupied atoms electrons can hop onto also decreases. This would imply the total energy decrease involved in this sort of hopping should also get smaller since the associated degrees of freedom are reduced. A larger value of ZT would be required to compensate the same Coulomb energy increase. This would result, as is observed in Figure 6.4, in a shift of the critical half-bandwidth ratio to larger values.
Deep in the conductivity region, when the effect of the Coulomb energy becomes small, the conductivity should tend to band theoretical results being smaller the farther away from \( n = 1 \). This is not observed since this single-site cluster theory predicts the conductivity to be the same for all \( 0.5 < n < 1.5 \) in the limit of infinite bandwidth. This is a peculiarity of the single-site cluster only.

1.4 Non-transitive region

The hopping and conductivity singularity does not occur for \( n < 0.5 \) or \( n > 1.5 \). This would indicate the lowering of hopping energy in producing doubly occupied sites could never overcome the Coulomb energy. The scarcity of possible occupied sites for electrons \((n < 1)\) and for holes \((n > 1)\) to hop on is responsible for this. Note that this does not agree with band theoretical results since there are doubly occupied sites in the limit \( ZT/I \to 0 \). In the analysis of Kanamori\(^{(17)}\) which is expected to prevail in the low electron or hole density regions or for large \( ZT/I \), the presence of doubly occupied sites is manifest. This would indicate the cluster approximation fails in this limit. Even so, the results of this theory are not to be totally rejected in these conditions. Even though there are presumably doubly occupied sites in narrow energy bands, their number would be so small for \( ZT/I \ll 1 \) so as to make our results acceptable. Moreover, the hopping per electron or hole is seen to increase continually as \( n \to 0 \) or \( n \to 2 \) whereas the conductivity decreases. This is physically correct. For smaller electron or hole concentrations, the phase space occupied by empty atoms is

* See Wilson\(^{(16)}\).
gradually chewing away from the one of occupied atoms. This means each
electron or hole has more room to hop in and so hopping increases. On the
other hand, because there are less particles to carry current, the conduc-
tivity decreases. Finally the linearity of the conductivity with the band-
width is as expected from band theory. The larger the bandwidth, the
larger the electron hopping contribution to the energy and thus the larger
the transport properties such as conductivity. This reasoning explains this
linearity for all occupancies.

2. $B = \omega$ Magnetic Properties

2.1 Ferromagnetism

As is shown in Figure (6.5), this single-site cluster theory predicts
a magnetic ground state, except for the half-filled band case. That it
should not be magnetized for $n = 1$ was shown early by Slater$^{(18)}$ and
recently by Kemeny$^{(19)}$. That it is magnetized for $n \neq 1$ is not surprising
considering the polarized reservoir approximation implicit in this theory
was expected to magnetically bias the cluster. The cluster is totally
magnetized below the critical transition point. Past this point, the
magnetization for $0.5 < n < 1.5$ is gradually reduced with increasing $Z/I$
down to an asymptotic limit. This limiting value is equal to that of a
saturated ferromagnet with $|n-1|$ electrons per site. In the limit
$Z/I \to \infty$ the system should not be magnetic as per Kanamori$^{(17)}$ and again
one sees this cluster theory breaks down at large bandwidth. This theory
also fails in the extreme occupancy limit $n \to 0.2$ as it had in its conduct-
ing properties. The low density calculations of Kanamori indicates our
Hamiltonian could not sustain ferromagnetism. This is also emphasized in the two-particle limit by the work of Slater and Koster (20).

The works of Hubbard (7), Gutzwiller (8), Nagaoka (21), and Penn (22), leave the room open for possible ferromagnetism in the intermediate density region \( n \lesssim 1 \). The general contention from Gutzwiller, Hubbard, Kanamori and Penn is that this Hamiltonian might give a ferromagnetic ground state provided \( ZT/I \) is small, \( n \lesssim 1 \) and the density of states at the Fermi level be large. Nagaoka's results are restricted to the case \( ZT/I \rightarrow 0 \) and they show the ground state to be ferromagnetic for \( n \lesssim 1 \) \( (n \neq 1) \). The face centered and hexagonal close-packed structures are quaint exceptions in that they are saturated ferromagnets for \( n \gtrsim 1 \) and paramagnets for \( n \lesssim 1 \). Of course, such structure dependence could not be expected out of a single-site cluster theory. The conclusion is that the ground state in the localized region \( (ZT/I \ll 1, n \lesssim 1) \) might well be ferromagnetic as this theory predicts.

2.2 Magnetic susceptibility

The reciprocal susceptibility for the half-filled band is shown in Figure (6.6). For \( ZT/I < .5 \), that is in the insulator region, the susceptibility is infinite. It arises because the reservoir is zero in the insulating region and so the cluster behaves like a free atom. This effect disappears in the two-site cluster. In the conducting region, always at \( n = 1 \), the susceptibility decreases with increasing bandwidth. This is a band effect. The larger the hopping energy, the lesser the effect of a magnetic field. The density of states at the Fermi level decreases
with increasing bandwidth. Thus the number of electrons partaking in the 
susceptibility at the Fermi level is decreased with an equivalent reduction 
in the susceptibility.

3. **Thermal Behavior**

3.1 **Phase transition**

The temperature behavior of the conductivity for various occupations 
is plotted in Figures (6.7) to (6.11). All curves show a transition 
temperature at which the conductivity goes to zero. The magnetization 
simultaneously goes to zero at the same critical temperature. Beyond this 
temperature, the reservoir is zero and the cluster behaves like a free atom. 
This second order transition is normal for a ferromagnetic system. However 
that the conductivity also goes to zero at the critical temperature comes 
as a surprise. Granted, the conductivity was shown to go to zero like $\beta$ 
at high temperatures (See Section IV.2), but not this abruptly. Nonetheless, the fact that the conductivity has the general trend of decreasing 
at high temperatures is correct. That the current in and out of the cluster 
be zero past the critical temperature is a simple consequence of the reservoir 
being zero then. In this light, the result makes sense. This odd behavior 
is not due to the definition of the conductivity but rather to the cluster 
technique itself which results in free atomic behavior past the transition 
temperature.

In Figure (6.12), this critical temperature is plotted as a function 
of $ZT/I$. It definitely shows a direct relationship between $(\beta)_{c}^{-1}$ and the 
half-bandwidth $ZT/I$. The conductivity and the magnetization disappear at
a temperature roughly of the order of magnitude of the bandwidth. This is when the band population starts to spread out throughout the whole band \( n_k \sim 1 \). This general rule is somewhat disturbed as \( n \to 1 \) for \( ZT/I < .5 \) due to the strong localized behavior which upsets any band theoretical arguments such as the above. It also fails as \( n \to 0;2 \) where it foresees a much too small critical temperature.

3.2 Conductivity

Looking at the curves for \( .5 < n < 1.5 \) the conductivity is seen to increase initially before decreasing again as per the general trend. This effect is seen to be more marked the closer \( ZT/I \) is to the critical value \( (ZT/I)_c \). This is in reasonable agreement with a semi-conductor type representation of the energy spectrum as derived by Hubbard\(^3\). He arrived at the conclusion that for small bandwidth, the system's density of states would look like that of a semi-conductor with two bands separated by a gap. As the bandwidth increases, the gap decreases and the bands deform, flattening out on the inside. This goes on until the Mott transition occurs when the two bands merge into a single one. This is depicted in Figure (6.1).

Before the transition occurs, the electrons in the lower band could be thermally excited to the upper band. (the situation is reversed for holes). There should then be an initial increase in the conductivity since the excited electrons in the upper band are conducting better. This effect would be larger, the closer \( ZT/I \) gets to the critical value, i.e., the smaller the gap. This picture would also predict the relative increase to be largest for \( n = 1 \) because of the absence of any conduction in the ground state. But this is not observed. In fact, there is no increase. The
insulator remains an insulator. This comes somewhat as a shock since physically one would expect the excited states of this insulating ground state to be somewhat conducting. As a matter of fact, there must be higher energy conducting states. Therefore the insulator should show some signs of conductivity at non-zero temperatures. One can then conclude that the thermal behavior, at least for the conductivity, is suspect. Again this is a consequence of the cluster approximation. The calculations show that for fixed $\mu$, $ZT$, $I$, the hopping in the excited states is smaller or equal in magnitude to the ground state hopping. So if the ground state hopping is zero, as in the insulating case, then the hopping is also zero in all the cluster excited states. This is clearly wrong as per the above argument. At fixed $\mu$, $ZT$, $I$, the reservoir is found to decrease with increasing temperature. This automatically follows from the previous arguments. The inevitable conclusion is that the thermal behavior of this cluster is doubtful in view of the obviously wrong excitation spectrum.

4. Magnetic Susceptibility

4.1 Antiferromagnetism

The reciprocal susceptibility for a half-filled solid is in Figure (6.13). The remarkable part resides in the linear relationship between $\chi^{-1}$ and $\beta^{-1}$ below the critical temperature. This behavior is strongly reminiscent of an antiferromagnet in the paramagnetic state. This theory would then predict the system to be antiferromagnetically inclined for $n = 1$. This result will be strongly enhanced in the two-site cluster.
4.2 Ferromagnetic transition

The reciprocal susceptibility for other electronic populations is drawn quite generally in Figure (6.14). Above the critical temperature, the general behavior follows the usual pattern of a free atom as derived in Equation (5.7). At the critical temperature, the susceptibility goes discontinuously to infinity. This indicates the onset of a magnetically ordered phase. This is a second order phase transition although very different from the one generally associated with Heisenberg type ferromagnetism. In the latter case, the susceptibility goes continuously to infinity on the high temperature side of the Curie temperature. Although this theory predicts an unconventional susceptibility behavior at the critical temperature, it must be borne in mind that the thermal behavior of this theory is questionable.

4.3 High temperature limit

The high temperature susceptibility is very interesting inasmuch as it is exact to order $\beta$. This theory predicts the reservoir is zero above the critical temperature whereas it is shown in Appendix G that the susceptibility is independent of the hopping, (i.e., the reservoir) to order $\beta$ at high temperatures. The high temperature expression for the susceptibility follows from Equation (5.7). It is

$$\chi = \frac{n(2-n)\mu_0^\beta}{2[1 - \frac{1}{4} n(2-n)\beta]}$$  (6.1)
Fig 6-1  HUBBARD'S BAND REPRESENTATION OF THE MOTT TRANSITION
Fig 6-2  SINGLE-SITE CLUSTER $\beta = \infty$ RESERVOIR HOPPING

Fig 6-3  SINGLE-SITE CLUSTER $\beta = \infty$ CONDUCTIVITY
Fig 6-4  SINGLE - SITE CLUSTER $\beta = \infty$ CRITICAL HALF - BANDWITH RATIO
Fig 6-6  SINGLE-SITE CLUSTER $\beta = \infty$ RECIPROCAL SUSCEPTIBILITY FOR THE HALF-FILLED SOLID

Fig 6-7  SINGLE-SITE CLUSTER CONDUCTIVITY $\eta = 1$
Fig 6-8  SINGLE-SITE CLUSTER CONDUCTIVITY  η = .9 : 1.1

Fig 6-9  SINGLE-SITE CLUSTER CONDUCTIVITY  η = .75 : 1.25
Fig 6-10 SINGLE-SITE CLUSTER CONDUCTIVITY \( n = 0.5 : 1.5 \)

Fig 6-11 SINGLE-SITE CLUSTER CONDUCTIVITY \( n = 0.1 : 1.9 \)
Fig 6-12  SINGLE-SITE CLUSTER CRITICAL TEMPERATURE
Fig 6-13  SINGLE-SITE CLUSTER RECIPROCAL SUSCEPTIBILITY FOR THE HALF FILLED SOLID

Fig 6-14  SINGLE-SITE CLUSTER RECIPROCAL SUSCEPTIBILITY
This is a remarkable result since it shows the high temperature susceptibility of Hubbard's Hamiltonian exhibits a Curie law with a quasi-Curie temperature \( \beta_c^{-1} = \ln(2-n)/4 \) and an effective moment \( \mu_{\text{eff}} = \mu_0 n(2-n)/2 \). This is the type of behavior characteristic of a ferromagnetic substance as derived in the Weiss theory. However the high temperature susceptibility is misleading since it would indicate magnetic behavior with Curie temperature as given above. But whatever magnetic behavior this theory predicts, it is uncorrelated to this value.

PART B: HUBBARD'S HAMILTONIAN IN THE TWO-SITE CLUSTER APPROXIMATION

In view of the complexity of the calculations for the two-site cluster, most computations were performed for a single value of the coordination number \( Z \). Being generally accepted that cluster theories are more meaningful for structures with a larger number of nearest neighbors, the value of \( Z = 12 \) for the face centered cubic (F.C.C.) lattice was chosen. Let it suffice to say the results for other structures such as the simple cubic (S.C.) and the body-centered cubic (B.C.C.) will only differ by numerical factors. Since the purpose of this section is to observe the general behavior of a two-site cluster, this will do.

Looking at the graphical representation of the results in Figures (6.15) to (6.35), it is very apparent that those graphs that are common with the single-site cluster generally bear striking similarity to these within numerical constants. Therefore most of the analysis in the single-site cluster case will carry over to this case. We shall then only stress the interesting differences between them.
5. \( \beta = \infty \) Electrical Properties

5.1. Hopping

Although the reservoir hopping per electron \( <a>^2/n \) in Figure (6.15) has all the characteristics of the single-site cluster there is one capital difference in the magnitude of this hopping. It has the identical limit as \( n \to 0;2 \) but is down by a factor of 2 as \( n \to 1 \). The reason for this must be the following. The reservoir hopping term is a surface effect since in this nearest neighbor restricted hopping, only the cluster sites nearest the cluster's surface will contribute to this kind of hopping. As the cluster gets bigger, the surface to volume ratio decreases. When there are many particles in the cluster \( (n \to 1) \) only the surface particles partake in the reservoir hopping and as such one would expect this hopping per particle to be proportional to this surface to volume ratio. Thus \( <a>^2/n \) should decrease with increasing cluster size when there are many particles in the cluster.

On the other hand, when the average number of particles in the cluster is very small e.g. less than one particle in the cluster, particles when in the cluster will tend to stay close to the surface where they can more easily interact with the reservoir. One would expect that in this extremely low density limit, the hopping would be independent of the volume of the cluster and would only depend on the number of electrons. This implies \( <a>^2/n \) should remain approximately constant when \( n \to 0;2 \).

The above argument would explain the status of Figure (6.15). It would also indicate that as the cluster gets larger, the hopping for \( n \to 1 \) would decrease and eventually go to zero in the limit of an infinitely large cluster.
As a matter of fact, for an infinite cluster, this reasoning would lead to the conclusion that the reservoir is zero for any finite n. This is reasonable since the larger the cluster, the smaller the fluctuations and so the smaller the reservoir. In this limit the reservoir becomes superfluous since the solution to an infinite cluster would give the exact solution to the problem at hand.

5.2 Peripheral part of the conductivity

The zero temperature peripheral contribution to the conductivity is plotted in Figure (6.16). It is seen to behave somewhat similarly to the single-site cluster result except for the reduction in magnitude. Since this conductivity is directly related to the hopping \( <a>^2/n \), it is then natural that if this hopping is smaller because of the increased size of the cluster, then so should the conductivity. Again projecting to an infinitely large cluster, the natural conclusion is that this part of the conductivity should also go to zero for finite n. Thus the remarkable fact that this conductivity is of the same magnitude as the bulk part of the conductivity in Figure (6.17) is merely a coincidence.

Another discrepancy with the single-site cluster results needs be mentioned. In the large bandwidth limit \( ZT \gg 1 \), it is seen that the conductivity would now be larger as \( n \to 1 \). The single-site cluster degeneracy in the conductivity from \( .5 < n < 1.5 \) is now lifted. This limit now behaves more like band theoretical results (See Section VI.1.3). The cause is probably the short-range correlation brought by this larger cluster.

5.3 **Bulk part of the conductivity**

In this larger cluster it was possible to calculate the conductivity between the two-sites. This conductivity in Figure (6.17) behaves in a slight way like the peripheral conductivity. There are critical half-bandwidth ratios \( (ZT/L)_c \) which coincide with the peripheral conductivity ones and there is a general linearity between \( \sigma_B \) and \( ZT/L \), at least for \( n < .5 \) or \( n > 1.5 \). The conductor-conductor transition is still present although the insulator-conductor transition can no longer be so labelled. In the half-filled band case, \( n = 1 \), there is internal conductivity even though the reservoir is zero. This is so since the cluster then behaves like a diatomic molecule which has a non-zero conductivity in its singlet ground state.

One also observes that there is no longer any electron-hole symmetry as far as this conductivity goes. The conductivity is larger for \( .5 < n < 1 \) than for \( 1.5 > n > 1 \). The reason for this will become apparent when we look into the magnetic properties of the cluster.

Although it is not apparent in Figure (6.17) the bulk conductivity for \( n < 1 \) and \( n > 1.5 \) is very close to the free diatomic molecule case. If one solves this cluster putting the reservoir equal to zero, one obtains results very close to these. The reservoir then has little effect on the bulk contribution to the conductivity. This effect was calculated to be within 10% of the zero reservoir case.

The fact that there are now two contributions to the conductivity does pose as a problem for \( n = 1 \). In this case, below the transition point, \( \sigma_p = 0 \) while \( \sigma_B \) is finite. Is the cluster an insulator or not? One can only
give a tentative answer to this. The bulk conductivity is strictly internal to the cluster while the peripheral conductivity reflects the one between the cluster and the reservoir. It can be argued that the only way a current can get to flow through the system is if one can get a current flowing in and out of the cluster. This would then give more weight to the peripheral part of the conductivity. Since $\sigma_p = 0$, the cluster is isolated from the rest of the system and thus the system can be considered an insulator. With this interpretation, the Mott transition is preserved.

5.4 Critical transition point

The locus of the critical half-bandwidth ratio $(ZT/I)_c$ is plotted in Figure (6.18) while the critical ratio for the half-filled band is plotted as a function of the inverse number of nearest neighbors in Figure (6.19). Figure (6.18) is similar to that of the single-site cluster except for a shift. Figure (6.19) is more interesting since it shows the dependence of the Mott transition on the coordination number. Note that as $Z \to \infty$, the Mott transition would occur at the same value as for the single-site cluster. This is no surprise since all cluster theories go to the single-site cluster results as $Z \to \infty$. Jotting down a few numbers,

$$(ZT/I)_c = 0.67 \quad \text{S.C.}$$

$$(ZT/I)_c = 0.61 \quad \text{B.C.C.}$$

$$(ZT/I)_c = 0.56 \quad \text{F.C.C.}$$
These values can now be better compared to

\[(ZT/I)_c = 0.577 \quad \text{Hubbard}^{(3)}\]

\[(ZT/I)_c = 0.63 \quad \text{Kemeny}^{(6)} \text{ for S.C.}\]

Hubbard's value compares favorably with the F.C.C. result while Kemeny's does with the S.C. result. The effect of correlation brought about by a larger cluster lifted the degeneracy in the Mott transition relative to crystal structure and brought the results closer to existing ones.

6. \(8 = \infty\) Magnetic Properties

6.1 Ferromagnetism

The ground state magnetization per site is plotted in Figure (6.20). For \(n > 1\) and \(n < 0.5\) there are no qualitative differences between this result and the single-site cluster one. However for \(0.5 < n < 1\) the magnetization is no longer saturated but is always equal to what was previously labelled the infinite bandwidth limit, i.e., \(|n-1|\) Bohr magneton per site. This is perhaps the most dramatic result of the short-range correlation effects.

This magnetic ground state is the one found by Nagaoka\(^{21}\) for the F.C.C. and hexagonal close packed structures, i.e., in the limit \(ZT/I \to 0\) the solid is totally magnetized for \(N/2 + 1\) electrons and paramagnetic for \(N/2 - 1\) electrons in the system. \(N\) is the total number of sites in the system.

Even though this theory would predict an identical ground state for the S.C. and B.C.C. structures, it is nevertheless gratifying to observe the effect in such a crude approximation as this one. It is this difference in electron-hole ground states which is responsible for the difference in the bulk part
of the conductivity. For \( n > 1 \), the ground state is magnetically saturated below the conductor-conductor transition while it is only partially so for \( n < 1 \). Thus the conductivity for \( n < 1 \) is larger because of the higher conductivity of the contributing singlet for \( n < 1 \) over the triplet for \( n > 1 \). This difference is not present in the peripheral part of the conductivity since the reservoir hopping does not seem to be influenced by this internal differentiation. The natural tendency for the free diatomic molecule, i.e., for zero reservoir, would be non-magnetic and this would reflect itself in the conductivity. The bulk conductivity for \( n \gtrsim 1 \) would be very close to that observed for \( n \lesssim 1 \). The presence of the reservoir has the drastic effect of favoring the magnetically saturated state for \( n > 1 \) over the partially saturated one which would be natural for the free molecule. This explains why it is only in the region \( 1 < n < 1.5 \) that the internal conductivity is so much different from the free molecule's.

6.2 Magnetic susceptibility

The zero temperature reciprocal susceptibility is shown in Figure (6.21) for the half-filled band case. In the conducting region it behaves like a conductor as pointed out in the single-site cluster results. However, in the insulating range, the susceptibility is now zero. This results from the singlet type ground state of the molecule when \( n = 1 \). It has zero susceptibility.

7. Temperature Dependence of the Conductivity

The peripheral conductivity in Figures (6.22) to (6.25) behaves just as it did for the single-site cluster while the internal conductivity in
Figures (6.26) to (6.30) behaves very much like the free diatomic molecule. As was pointed out previously, the major difference is in the reduced bulk conductivity below the transition temperature of Figure (6.31) for $1 < n < 1.5$ (compare the conductivity for $n = .9$ to that for $n = 1.1$).

The transition is characterized by a slight discontinuity, often unnoticeable, in the slope of the bulk conductivity. After the critical temperature has been reached, the reservoir is zero and the conductivity is strictly that of the free molecule. It is seen to be non-zero and to decrease proportionally to $\beta$ at high temperatures as predicted in Section IV.2.

The bulk conductivity is definitely more physical in its thermal behavior. The reason is that it is much less affected by the reservoir and even though the excited states for the reservoir may be way off, those within the cluster are correct. It might be worthwhile to comment on the bulge in the internal conductivity at low temperature for $n = 1$. The conductivity initially decreases very fast but suddenly it levels off or may even increase slightly before going down again in the characteristic high temperature fashion. This "second wind" in the conductivity occurs because of the large conducting possibilities of the higher energy cluster states involving one and three electrons. Were these states very close to the ground state, the conductivity might increase initially at $\beta \rightarrow \infty$. But they are at much higher energy and the thermodynamic weight to these states is so small that the effect is reduced to a bulge in the conductivity. One may also add that the initial increase observed in the peripheral conductivity is not found
in the internal one. The reason is again that the reservoir has little

effect on this internal property. The natural tendency at low tempera-
tures is for a sharp decrease in the conductivity, so sharp that even though
the reservoir would tend to pull it back up a bit, it does not succeed.

8. Magnetic Susceptibility

Definitely the most worthwhile comment to pass on the magnetic
behavior is to the inverse susceptibility curves for \( n = 1 \) in Figure (6.32).
This shows the reciprocal susceptibility in the insulating region and it
indicates the system is definitely antiferromagnetic and not only so
inclined as from Figure (6.33). This then validates the second order
perturbation theory of Mattis \(^{(2)}\) which shows the kinetic hopping term
effectively reduces to an antiferromagnetic exchange interaction between
electrons on neighboring sites. This perturbation approach would be expected
to be valid for \( n \cong 1 \) and \( ZT/I \ll 1 \) and it seems to be. This kinetic ex-
change is proportional to \( T^2 \). From simple Weiss field theory it is easily
shown that the resulting Neel temperature \( (\beta_N)^{-1} \) should be proportional to
this exchange, i.e., to \( T^2 \). This is, indeed, observed as pointed out in
Figure (6.32). This antiferromagnetic ground state is also deduced by
Kemeny \(^{(23)}\) using more sophisticated arguments.

9. Free Energy Considerations

Thus far, our attention has been focused on the thermodynamics at
constant \( ZT \). From the definition of \( T \) as in Hubbard \(^{(3)}\),

\[ T = \int dt \, W(\mathbf{r} - \mathbf{R}_i) \left[ -\frac{\mathbf{v}^2}{2m} + V(r) \right] W(\mathbf{r} - \mathbf{R}_j) \]

\[ W(\mathbf{r} - \mathbf{R}_i) = \text{Wannier function centered on site } i \]
\[ j = \text{nearest neighbor to } i \]
\[ V(r) = \text{crystal potential} \]

It is evident that \( T \) is related to the interatomic distance \( a \). The smaller \( a \) is, the larger \( T \). For fixed interatomic distance, \( T \) is also fixed. This means our study has so far been performed at constant volume. This is a bit unrealistic since experimentally one usually works at constant pressure. At constant pressure, one should look for the interatomic distance, i.e., the ZT which minimizes the Gibbs free energy \( G \). At zero pressure

\[ G = \text{Helmholtz free energy} = -\ln P/\beta \]

This idea has been carried out for the two-site cluster for \( n = 1 \). The free energy has been calculated as a function of ZT for fixed temperatures. The results are shown in Figure (6.34) where the free energy is plotted as a function of \(-\ln|\text{ZT/I}|\). The reason for this plot is that in the tight-binding approximation, the interatomic distance is related to ZT in roughly the following way:

\[ T \propto e^{-a} \quad \text{or} \quad a \propto -\ln|T| \]

The abscissa of Figure (6.34) is thus closely related to \( a \). This plot is very interesting. It shows that at a given temperature the free energy is

---

*See Slater(33), Volume 1, Chapter 3.*
approximately constant for values of ZT/I under a critical point. This is when the reservoir is zero. But as soon as ZT/I gets above this critical value, i.e., as soon as the interatomic distance is reduced past a critical value, the reservoir is turned on and the free energy drops very fast. Since the hopping is proportional to the slope of the free energy, this means the hopping is negligible under the critical point and gets large above. This type of behavior is indicative of a phase transition. The Mott transition discussed at length previously is just this phase transition from negligible hopping (insulator) to large hopping (conductor).

Note that the free energy decreases continuously as a gets smaller. This means the binding energy gets larger. In order to prevent the lattice from collapsing, the nuclear interaction must be added. The lattice contribution to the free energy would be proportional to the reciprocal interatomic distance. If one adds such a repulsive energy (dotted line in Figure 6.34) to the binding energy, the total free energy would look somewhat as in Figure (6.35). At low temperatures the minimum in free energy (dotted line in Figure (6.35) would shift to larger lattice constants with increasing temperatures. Thus thermal expansion. However as the temperature gets larger, there comes a point at which the free energy for infinite lattice constant (T = 0) becomes lowest. There is then a first-order phase transition at that point because of the discontinuous first derivative of the free energy with respect to temperature. The lattice wants to expand to infinity meaning the solid-state is unstable towards a fluid state transformation. Since we have not considered the possibility of short-range
internuclear energy it is not possible to state whether the transition is
to a liquid or gasous phase. Let it suffice to say the solid becomes unstable at
that critical temperature under zero pressure conditions.

This result is extremely interesting in that the solid will break up
before the reservoir can turn off. This makes for a much better thermal
behavior. One then sees that this cluster model has all the essence of
physical reality. Thermal expansion and even melting can be accounted
for.

10. Summary and Conclusions

In the light of the results from the single-site and the two-site
cluster theories, we are in a position to make the following statements
about the results and the theory.

a) The theory is generally acceptable for localized problems in the
ground state. It seems to fail somewhat miserably at large bandwidths and
less so in the extreme occupancy limits n \to 0;2. The thermal behavior of
the reservoir at constant volume is dubious, and as such, care should be
given to those thermal properties that depend on the reservoir to a large
extent.

b) This cluster theory predicts a Mott insulator-conductor transition
for the half-filled cluster at values comparable to those obtained by more
sophisticated theories. It also predicts a conductor-conductor transition
for average electronic occupancies per site of .5 \leq n \leq 1.5.
c) This theory also predicts ferromagnetism for \( n \neq 1 \) with a Nagaoka type ground state below the conductor transition point, i.e., magnetic saturation for \( n > 1 \) and partial magnetization \((1-n)\) Bohr magneton for \(.5 < n < 1\). This magnetization disappears at a critical temperature.

d) At this critical temperature the constant volume second order phase transition is highly unconventional. The susceptibility discontinuously goes to infinity on the high temperature side of the transition. This result must, however, be weighed in view of the probable failure of the theory to predict correct constant volume thermal behavior on such a reservoir dependent quantity.

e) The high temperature limit yields the exact result that the susceptibility behaves like that of a ferromagnetic substance in its high temperature paramagnetic state. The resulting quasi-Curie temperature seems uncorrelated to any predicted magnetic behavior of the Hamiltonian.

f) The half-filled cluster is found to be antiferromagnetic in the insulating region. This is in accord with Mattis' kinetic exchange theory. The susceptibility in the conducting region behaves in a way similar to an antiferromagnet in the paramagnetic state.

g) It was found that the effect of the reservoir decreases with increasing cluster size. One would then have to go to larger clusters in order to diminish the influence of the reservoir on the thermal behavior of the system.
Fig 6-15  TWO-SITE CLUSTER $\beta = \infty$ RESERVOIR HOPPING

Fig 6-16  TWO-SITE CLUSTER $\beta = \infty$ PERIPHERAL PART OF THE CONDUCTIVITY
Fig 6-17 TWO-SITE CLUSTER $\beta = \infty$ BULK PART OF THE CONDUCTIVITY
**Fig 6-18**  TWO-SITE CLUSTER $\beta = \infty$ CRITICAL HALF-BANDWITH RATIO

**Fig 6-19**  TWO-SITE CLUSTER $\beta = \infty$ COORDINATION NUMBER DEPENDENCE OF THE CRITICAL HALF-BANDWITH RATIO FOR THE HALF FILLED BAND
Fig 6-20 TWO-SITE CLUSTER $\beta = \infty$ SPONTANEOUS MAGNETIZATION
Fig 6-21  TWO-SITE CLUSTER $\beta = \infty$ RECIPROCAL SUSCEPTIBILITY FOR THE HALF-FILLED SOLID
\[ q_p = 0 \text{ for } \frac{ZT}{I} < \left( \frac{ZT}{I} \right)_0 \]

\[ \frac{1}{\beta I} \]

**Fig 6-22** TWO-SITE CLUSTER PERIPHERAL PART OF THE CONDUCTIVITY \( n = 1 \)

\[ \frac{1}{\beta I} \]

**Fig 6-23** TWO-SITE CLUSTER PERIPHERAL PART OF THE CONDUCTIVITY \( n = 0.9 : 1.1 \)
**Fig 6-24** TWO-SITE CLUSTER PERIPHERAL PART OF THE CONDUCTIVITY $n = 0.5:1.5$

**Fig 6-25** TWO-SITE CLUSTER PERIPHERAL PART OF THE CONDUCTIVITY $n = 0.1:1.9$
Fig 6-26  TWO-SITE CLUSTER BULK PART OF THE
CONDUCTIVITY  n = 1

Fig 6-27  TWO-SITE CLUSTER BULK PART OF THE
CONDUCTIVITY  n = .9
Fig 6-28  TWO-SITE CLUSTER BULK PART OF THE CONDUCTIVITY  \( n = 1.1 \)

Fig 6-29  TWO-SITE CLUSTER BULK PART OF THE CONDUCTIVITY  \( n = 0.5 : 1.5 \)
Fig 6-30  TWO-SITE CLUSTER BULK PART OF THE CONDUCTIVITY  $n = 0.1 : 1.9$

Fig 6-31  TWO-SITE CLUSTER CRITICAL TEMPERATURE
Fig 6-32  TWO-SITE CLUSTER RECIPROCAL SUSCEPTIBILITY IN THE INSULATOR REGION (n = 1)
Fig 6-33 TWO-SITE CLUSTER RECIPROCAL SUSCEPTIBILITY
IN THE CONDUCTING REGION (n = 1)
Fig 6-34 ELECTRONIC FREE ENERGY AT CONSTANT TEMPERATURE
Fig 6-35  TYPICAL TOTAL FREE ENERGY AT CONSTANT TEMPERATURE
**Fig 6-36**  THE IMPURITY $\beta = \infty$ RESERVOIR HOPPING

**Fig 6-37**  THE IMPURITY $\beta = \infty$ CRITICAL WIDTH PARAMETER
Fig 6-38  THE IMPURITY CRITICAL TEMPERATURE
h) The constant pressure behavior of the half-filled system would predict thermal expansion up to a fluidization temperature at which the system would go through a solid-fluid first-order phase transition.

PART C: ANDERSON'S HAMILTONIAN

11. $\beta = \infty$ Properties

11.1 Localized moment

The ground state behavior of the hopping between the impurity and the s-band is pictured in Figure (6.36). The hopping is seen to be zero up to a critical width parameter $\Delta c/\lambda$ after which it very sharply increases towards a saturation value. This implies that below this critical coupling, the impurity is predicted to be free or perfectly localized. Past this point, the hopping becomes very large and the impurity would lose part of its localized character. The surprising part is that when comparing the locus of this critical width parameter with that of Anderson, in Figure (6.37), the similarity between the two is striking. They even enclose identical areas (.25). This is, indeed, a peculiar result considering the two totally different approaches to the problem. Here it is the coupling which is approximated whereas it was the Coulomb term which Anderson approximated in a Hartree way.

In a simple minded way the physical idea of a localized moment makes sense. For a given value of $E_o$ below the chemical potential level, the only way the impurity electron can hop off the atom into the s-band is by making a transition from the impurity single-particle level to the higher energy chemical potential level. This is energetically unfavorable as long
as the loss in the coupling energy does not compensate for this gain. It would then be expected that this hopping should be strongly hampered and even prevented under a critical value of the coupling parameter $\Delta_o$. For larger values, hopping could and would increase because of the favorably larger coupling. On the other hand, hopping from the s-band onto the impurity could normally only be achieved at the expense of the Coulomb repulsion from two electrons on the impurity. This again is energetically unfavorable. It could be argued that there also exists a critical $\Delta_I$ at which the loss in coupling energy would be sufficient to overcome the Coulomb energy gain. There are then two mechanisms which compete in the hopping between the impurity and the s-band. Each of these is characterized by a critical $\Delta$. These need not be equal since the energies involved in the transfer are different.

\[
\begin{align*}
|\mu_o - E_o| & \quad \text{for the impurity + s-band transfer} \\
|\mu_o - E_o + I| & \quad \text{for the s-band + impurity transfer}
\end{align*}
\]

The one involving the smaller energy difference would probably win the competition and determine the critical point. Thus for $0 \leq E_o \leq 1/2$, the impurity + s-band mechanism would prevail. Because of the energy transfer involved, one would expect the critical point to increase as $E_o$ gets larger. This is observed. For $1/2 \leq E_o \leq I$, the s-band + impurity mechanism would dominate. Then the critical point would decrease with increasing $E_o$. This, again, is observed. Figure (6.37) is then in agreement with the physics of a localized moment using these simple arguments.
Even though the above arguments make sense, the idea of a sharp transition from totally localized to partially localized moment does not. Such sharp changes are highly unlikely (24) for a single impurity. Sharp changes are usually characteristic of cooperative phenomena. These are surely absent in the single impurity problem. One would expect a more gradual, a smoother transition. The cluster approach to the impurity problem is then probably out of line (and so would a Hartree approximation). It involves a bootstrap condition which is justifiable for cooperative phenomena only.

Moreover, the work of Schrieffer and Mattis (14) has shown that the impurity cannot be magnetic whenever there is a small average number of particles on the impurity. In the limit when this number is close to one and for small $\Delta/I$ the work of Schrieffer and Wolf (25) shows that the Anderson problem can be canonically transformed to a Kondo-type problem (26) with an effective antiferromagnetic exchange between the impurity electron and the $s$-band electrons. The work of Nagaoka (27), Hamann (28) and Suhl (29) shows the Kondo impurity to be non-magnetic since this kinetic exchange leads to a singlet type ground state between the impurity electron and the neighbor ones in the $s$-band. The general contention (30) is then that the Anderson impurity is non-magnetic. This again sheds some doubt as to the validity of the cluster approximation to this single-impurity problem.

11.2 Hopping region

Unfortunately, because of the complexity of the $s$-band Hamiltonian when the reservoir is non-zero, the system still remains unsolved under non-zero reservoir conditions.
12. **High Temperature Limit**

The temperature at which the reservoir disappears altogether can be obtained. It is shown in Figure (6.38). For higher temperatures, the reservoir is zero. The impurity again decouples identically from the s-band. The solution to the impurity can be written down. From Section V.1.2, we infer that

\[
P = 1 + 2e^{-\beta E_0} + e^{-\beta(2E_0 - I)}
\]

\[
n = 2(e^{-\beta E_0} + e^{-\beta(2E_0 - I)})/P
\]

\[
x = 2\mu_0^2 e^{-\beta E_0}/P
\]

All the above are impurity quantities.

In the limit of very high temperatures when \(\beta I \ll 1\), the result becomes exact to order \(\beta\) (from Appendix G).

\[
n \sim 1
\]

\[
x = \frac{\mu_0^2}{2}(\beta^{-1} - I)/4
\]

Again this bears close similarity with the high temperature expansion limit of the Hubbard Hamiltonian. The impurity susceptibility shows a Curie law behavior with Curie temperature \(\beta_{c}^{-1} = I/4\) and effective moment \(\mu_0/2\). This is the behavior of the impurity at high temperature and from it, one cannot draw any conclusions as to the magnetic properties at low temperatures.
13. **Summary and Conclusions**

The following statements can now be made as to the theory and its results.

a) This cluster theory does not seem to be applicable to a single-impurity problem at least at low temperatures. It seems only justified for translationally invariant systems where cooperative effects can take place.

b) This theory predicts a totally localized moment in the ground state within a region of parameters similar to that of Anderson for the magnetic moment.

c) However this approach did give the correct information that the chemical potential is controlled by the s-band and is essentially unperturbed. The hopping from the impurity to the s-band occurs only at the chemical potential level in the latter.

d) The high temperature limit is exact and indicates this type of impurity would have a susceptibility with Curie temperature at I/4, and an effective moment of $\mu_0/2$. 
CHAPTER VII

CONCLUSION

The self-consistent cluster approximation is well what it was intended to be: a simple yet reasonable approach to narrow energy band problem. It was seen to fail precisely in regions where the band properties would be predicted to take over the localized ones and it was successful in regions of localized character as far as translationally invariant systems are concerned. The effect of added correlation brought about by larger cluster sizes was seen to be highly beneficial to the results. The major setbacks seem to be in the thermal behavior of small clusters at constant volume and the relative lack of applicability to single-impurity problems.

This is by no means meant to be the final work on the subject. Much could still be done to try and remedy the annoying drawbacks of the theory. Much more could also be done on the constant pressure properties of the system. This promising aspect was but lightly brushed in this work.

This theory could conceivably be applied to more involved Hamiltonians such as those obtained by adding exchange to Hubbard's Hamiltonian or considering degenerate or multiple bands. It could also be applied to alloy problems or even the liquid-solid phase transition.
APPENDIX A

Long-Range Limit of the Thermodynamic Hopping Average

Fourier transforming the hopping average in reciprocal \( \mathbf{k} \) space:

\[
\langle a_{\delta \sigma}^+ a_{1\sigma} \rangle = \frac{i\mathbf{k} \cdot (\mathbf{R}_\delta - \mathbf{R}_1)}{N^{-1} \sum_{\mathbf{k}} \langle n_{k\sigma} \rangle e^{i\mathbf{k} \cdot (\mathbf{R}_\delta - \mathbf{R}_1)}
\]

where \( \mathbf{k} \) = vector in first Brillouin zone.

\((\mathbf{R}_\delta - \mathbf{R}_1)\) = vector distance between sites 1 and \( \delta \).

\(\langle n_{k\sigma} \rangle\) = thermodynamic average of the electronic occupancy of the \( k \) state with spin \( \sigma \).

\(N\) = total number of sites in the system.

As \( |\mathbf{R}_\delta - \mathbf{R}_1| \to \infty \), the phase factor \( e^{i\mathbf{k} \cdot (\mathbf{R}_\delta - \mathbf{R}_1)} \) oscillates so rapidly with \( \mathbf{k} \) that essentially each half cycle cancels the preceding one. The net value of the summation goes to zero.

\[
\lim_{|\mathbf{R}_\delta - \mathbf{R}_1| \to \infty} \langle a_{\delta \sigma}^+ a_{1\sigma} \rangle = 0
\]

*See Kittel(31) for such a transformation.
APPENDIX B

Symmetries in Hubbard's Hamiltonian

\[ \mathcal{H} = \sum_{\sigma, i} \sum_{\sigma} T_{ij} a_{i \sigma}^+ a_{j \sigma} + \sum_{\sigma, i} n_{i \sigma} - \mu \sum_{\sigma} \Sigma n_{i \sigma} \]

B.1) Spin symmetry

A.) Spin rotation operator

The spin rotation operator is found in Messiah \(^{32}\) to be

\[ R = e^{-i \phi \sum_{j} \hat{\sigma} \cdot \hat{k}} \]

where \( \phi \) is the angle of rotation around the unitary axis \( \hat{k} \)

\( \hat{\sigma} \) is the Pauli spin vector \( \hat{\sigma} = 2\hat{s} \)

\[ \sigma_{jx} = (a_{j}^+ a_{j} + a_{j}^+ a_{j}^+) \]

\[ \sigma_{jy} = (a_{j}^+ a_{j} - a_{j}^+ a_{j}^+) / i \]

\[ \sigma_{jz} = (n_{j}^+ - n_{j}^+) \]

The summation over "j" extends to all sites. This operator can be rewritten as

\[ R = \bigotimes_{j} e^{i \phi \sigma_{j} \cdot k} \]

where \( \bigotimes_{j} \) indicates a tensor product over all site subspaces.
Because of the following property

\[ \sigma_{jk}^{(2p)} = n_j^+ + n_j^- - 2n_j^+ n_j^- \]

\[ \sigma_{jk}^{(2p+1)} = \sigma_{jk} \]

the rotation operator becomes:

\[ R = \bigotimes_j \left[ 1 - (n_j^+ + n_j^- - 2n_j^+ n_j^-)(1 - \cos \phi/2) - i\sigma_{jk} \sin \phi/2 \right] \]

Under a rotation, any Hamiltonian becomes

\[ \mathcal{H}' = R \mathcal{H} R^+ \]

B.) Rotated Hamiltonian

It can be shown, after a lengthy but elementary operator manipulation, that under such a transformation

\[ R_{a_j^+} R^+ = A a_j^+ + B a_j^+ \]

\[ R_{a_j^-} R^+ = B^* a_j^+ - A^* a_j^+ \]

\[ |A|^2 + |B|^2 = 1 \]

where the exact expressions for A, B depend on the angle \(\phi\) and the orientation of the rotation axis \(\hat{k}\). Notice that this transformation preserves the anti-commutation rules of these operators. Moreover, under the same rotation:
\[ R(\Sigma a_i^+ a_j)R^+ = \Sigma a_i^+ a_j^+ \]
\[ R(\Sigma n_i)R^+ = \Sigma n_i R^+ \]
\[ Rn_{i+}n_{i+}R^+ = n_{i+}n_{i+} R^+ \]

Substituting these various expressions back into Hubbard's Hamiltonian
\[ RH = H' \]
and it is invariant under spin rotation.

B.2) **Time Reversal Symmetry**

A.) **Time Reversal Operator**

The time reversal operator, as given in Messiah, is
\[ T = \frac{-1}{2} i \pi \sum_j j y K_0 \]
\[ T^+ T = TT^+ = 1 \]

where \( K_0 \) is the conjugation operator \( K_0^2 = 1 \). Following the analysis in Part A of the previous section,
\[ T = \otimes_j [1 - (n_j^+ n_j^+ - 2n_j^+ n_j) - (a_j^+ a_j^+ - a_j^+ a_j)] K_0 \]

Any time reversed Hamiltonian becomes
\[ H' = TH T^+ \]
B.) **Time Reversed Hamiltonian**

After some operator manipulation, such a transformation yields

\[
T(a^+_{j+})T^+ = K_o a^+_{j+}K_o = a^+_{j+}
\]

\[
T(a^+_{j+})T^+ = -K_o a^+_{j+}K_o = -a^+_{j+}
\]

\[
T(a^+_{i+}a^-_{j+})T^+ = K_o a^+_{i+}a^-_{j+}K_o = a^+_{j+}a^-_{i+}
\]

\[
T(n^-_{j+})T^+ = n^-_{j+}
\]

\[
T(n^-_{j+}n^+_{j+})T^+ = n^-_{j+}n^+_{j+}
\]

It is then apparent that

\[
T\mathcal{H}T^+ = \mathcal{H}
\]

and the Hamiltonian is invariant under time reversal.
APPENDIX C

Thermodynamic Invariance Under Canonical Transformation

Consider the following canonical transformation

\[ A^+ A = AA^+ = 1 \]

Under its effect a Hamiltonian becomes

\[ H' = AHA^+ \]

The partition function is then

\[ -\beta H \]

\[ P = Tr(e^{-\beta H}) \]

Because of the unitarity of this transformation

\[ -\beta H \]

\[ P = Tr(e^{-\beta AHA^+}) \]

Because of the invariance of the trace under cyclic permutation of the operators

\[ -\beta H \]

\[ P = Tr(Ae^{-\beta AHA^+}) \]

But then

\[ Ae^{-\beta AHA^+} = \sum_{n=0}^{\infty} \frac{-\beta H}{n!} \]

\[ \sum_{n=0}^{\infty} \frac{-\beta AHA^+}{n!} \]

\[ = e^{-\beta H'} \]
and so

\[-\beta \mathcal{H} \quad \text{and} \quad -\beta \mathcal{H}'\]

\[P = \text{Tr}(e^{-\beta \mathcal{H}}) = \text{Tr}(e^{-\beta \mathcal{H}'}) = p'\]

The partition function is then unchanged by any canonical transformation. Similarly, any operator average is unaltered by this transformation:

\[\langle 0 \rangle = \frac{\text{Tr}(e^{-\beta \mathcal{H}})}{p} = \frac{\text{Tr}(e^{-\beta \mathcal{H} + A^+A})}{p'}\]

\[= \frac{\text{Tr}(e^{-\beta \mathcal{H}'})}{p'} = \frac{\text{Tr}(e^{-\beta \mathcal{H} + A^+A})}{p'}\]

\[= \frac{\text{Tr}(e^{-\beta \mathcal{H}'})}{p'} = \frac{\text{Tr}(e^{-\beta \mathcal{H} + A^+A})}{p'}\]

\[= \langle A^+A^+ \rangle\]

\[Q.E.D.\]
Symmetries in Anderson's Hamiltonian

\[ \mathcal{H} = \sum_{\sigma} \sum_{\mathbf{k}} (\epsilon_{\mathbf{k}} - \mu) n_{\mathbf{k}\sigma} + \sum_{\mathbf{k}} \sum_{\mathbf{k}' \sigma} (a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}'\sigma} + a_{\mathbf{k}'\sigma}^+ a_{\mathbf{k}\sigma}) \]

\[ + \ i \ n_{0\uparrow} n_{0\downarrow} - (E_0 + \mu) n_{0\uparrow} \]

D.1) Spin Symmetry

A.) Spin rotation operator

The spin rotation operator being

\[ R = e^{\frac{i}{2} \left( \sum_{\mathbf{k}} \mathbf{\sigma}_{\mathbf{k}} \right)} \]

it can be rewritten as

\[ R = e^{\frac{i}{2} \mathbf{\sigma}_{\mathbf{K}}} \otimes e^{-\frac{i}{2} \mathbf{\sigma}_{\mathbf{K}}} \]

with

\[ \sigma_{\alpha\sigma} = (a_{\alpha\sigma}^+ a_{\alpha\sigma} + a_{\alpha\sigma}^+ a_{\alpha\sigma}) \]

\[ \sigma_{\alpha} = (a_{\alpha\uparrow}^+ a_{\alpha\downarrow}^+ + a_{\alpha\downarrow}^+ a_{\alpha\uparrow}) / i \quad \alpha = 0; \mathbf{K} \]

\[ \sigma_{az} = (n_{\alpha \uparrow} - n_{\alpha \downarrow}) \]
Since

\[ \sigma_{aK}^{(2p)} = n_{a\uparrow} + n_{a\downarrow} - 2n_{a\uparrow} n_{a\downarrow} \]

\[ \sigma_{aK}^{(2p+1)} = \sigma_{aK} \]

\[ R = [1 - (n_{o+} + n_{o-} - 2n_{o+} n_{o-}) (1 - \cos \phi/2) - i \sigma_{oK} \sin \phi/2] \]

\[ \times \bigotimes_{k} [1 - (n_{k\uparrow} + n_{k\downarrow} - 2n_{k\uparrow} n_{k\downarrow}) (1 - \cos \phi/2) - i \sigma_{kK} \sin \phi/2] \]

B.) Rotated Hamiltonian

The rotated Hamiltonian is

\[ \mathcal{H}' = R \mathcal{H} R^+ \]

Since

\[ R(\Sigma a_{k\sigma}^+ a_{o\sigma})^+ R^+ = \Sigma a_{k\sigma}^+ a_{o\sigma}' \]

\[ R(\Sigma n_{o\sigma})^+ R^+ = \Sigma n_{o\sigma}' \]

\[ R(n_{o+} n_{o-})^+ R^+ = n_{o+}' n_{o-}' \]

it is easily verified that \( \mathcal{H}' = \mathcal{H} \) and that it is invariant under spin rotation.
D.2) Time Reversal Symmetry

A.) Time reversal operator

The time reversal operator is

\[ T = e^{-\frac{1}{2} i \pi \sum_\kappa} \otimes e^{-\frac{1}{2} i \pi \sum_{\kappa} \kappa} \]

which can be rewritten as

\[ T = [1 - (n_{\kappa} + n_{\kappa} - 2n_{\kappa} n_{\kappa} - a_{\kappa} a_{\kappa} + a_{\kappa} a_{\kappa})] \]

\[ \otimes [1 - (n_{\kappa} + n_{\kappa} - 2n_{\kappa} n_{\kappa} - a_{\kappa} a_{\kappa} + a_{\kappa} a_{\kappa})] \]

B.) Time reversal hamiltonian

Under time reversal

\[ T(a_{\alpha}^{+})T^{+} = a_{\alpha}^{+} \]

\[ T(a_{\alpha}^{+})T^{+} = -a_{\alpha}^{+} \]

\[ T(a_{\kappa}^{+} a_{\sigma}^{+})T^{+} = a_{\sigma}^{+} a_{\kappa}^{+} \]

\[ T(n_{\alpha\sigma})T^{+} = n_{\alpha\sigma} \]

\[ T(n_{\kappa}^{+} n_{\kappa}^{+})T^{+} = n_{\kappa}^{+} n_{\kappa}^{+} \]

It is then apparent that \( THT^{+} = H \), which proves the invariance of \( H_{o} \) to \( T \).
APPENDIX E

Invariance of the Average Occupation Number to First Order in the Magnetic Field

In the presence of a magnetic field any system would be characterized by

\[
\langle n_i \rangle = \frac{\beta (H_o - \mu H \Sigma(n_{a^+} - n_{a^+}))}{\text{Tr}[e^{-\beta (H_o - \mu H \Sigma(n_{a^+} - n_{a^+})}]}
\]

where \(\{a\}\) are the characteristic quantum numbers of the system.

As \(H \to 0\), using the result of the perturbation analysis of Section 1V.1,

\[
\langle n_i \rangle = \langle n_i \rangle_0 + H \int_0^\beta \text{Tr}[e^{-\beta (H_o - \mu H \Sigma(n_{a^+} - n_{a^+})} - H_o] (n_i - \langle n_i \rangle_0) \rangle_0
\]

+ ....

where the suffix \(o\) refers to averages at \(H = 0\).

If \(H_o\) is invariant to spin inversion \(I\),

\[
\langle e^{H_o} \Sigma(n_{a^+} - n_{a^+}) e^{-H_o} (n_i - \langle n_i \rangle) \rangle_0
\]

\[
= \langle e^{H_o} \Sigma(n_{a^+} - n_{a^+}) e^{-H_o} (n_i - n_i \rangle_0 I^+ \rangle_0
\]

\[
= \langle e^{H_o} \Sigma(n_{a^+} - n_{a^+}) e^{-H_o} (n_i - n_i \rangle_0
\]

\[
= -\langle e^{H_o} \Sigma(n_{a^+} - n_{a^+}) e^{-H_o} (n_i - n_i \rangle_0
\]

\[
= 0
\]
Thus, to first order in $\mathcal{H}$, $\langle n_1 \rangle = \langle n_1 \rangle_0$ independently of any other properties of $\mathcal{H}_0$. 
APPENDIX F

Electrical Energy and the Current Operator in Second Quantization

F.1) Second Quantization Rules

The general rule for finding the occupation space representation of any configuration space operator \( \Theta \) of the general form

\[
\Theta(x) = \sum V(x_i) + \sum V(x_i x_j) + \sum V(x_i x_j x_k) + \ldots
\]

\[i \neq j \neq k\]

where \( x \) can involve the spatial coordinate \( \vec{r} \) as well as the momentum \( \vec{p} \) and \( i \) refers to a specific electron in the many electron system.

(These terms in \( \Theta(x) \) each represent single-body, two-body, three-body interactions, respectively) is the following (4)

\[
\Theta = \int d\vec{r} \psi^+(\vec{r}) V(x) \psi(\vec{r})
\]

\[+ \int d\vec{r}_1 d\vec{r}_2 \psi^+(\vec{r}_1) \psi^+(\vec{r}_2) V(x_1 x_2) \psi(\vec{r}_2) \psi(\vec{r}_1)
\]

\[+ \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \psi^+(\vec{r}_1) \psi^+(\vec{r}_2) \psi^+(\vec{r}_3) V(x_1 x_2 x_3) \psi(\vec{r}_3) \psi(\vec{r}_2) \psi(\vec{r}_1)
\]

\[+ \ldots \ldots \]

The destruction operator \( \psi(\vec{r}) \) and the creation operator \( \psi^+(\vec{r}) \) satisfy the anticommutation rules.

\[
\{ \psi(\vec{r}_1), \psi^+(\vec{r}_2) \} = \delta(\vec{r}_1 - \vec{r}_2)
\]

\[
\{ \psi(\vec{r}_1), \psi(\vec{r}_2) \} \quad \{ \psi^+(\vec{r}_1), \psi^+(\vec{r}_2) \} = 0
\]
As it is customary in tight binding problems, these operators are expanded in occupation space in a complete set of Wannier states

\[ \psi(\mathbf{r}) = \sum_{\mathbf{k}, i, \sigma} \phi_{k}^{(\mathbf{r}-\mathbf{R}_i)} a_{i\mathbf{k}\sigma} \]

where \( i, \mathbf{k}, \sigma \) are the site, band and spin quantum numbers, respectively, and \( a_{i\mathbf{k}\sigma} \) is the destruction operator of an electron of spin \( \sigma \) on site \( i \) in the band \( \mathbf{k} \).

F.2) Properties of the Wannier Functions

A.) The Wannier functions are orthonormal

\[ \int d\mathbf{r} \phi_{\mathbf{k}, 1}^{*}(\mathbf{r}-\mathbf{R}_i) \phi_{\mathbf{k}, 2}(\mathbf{r}-\mathbf{R}_j) = \delta_{\mathbf{k}, 1} \delta_{\mathbf{k}, 2} \delta_{ij} \]

B.) The Wannier functions can be expanded into Bloch functions \( \phi_{\mathbf{kK}}(\mathbf{r}) \)

\[ \phi_{\mathbf{k}}(\mathbf{r}-\mathbf{R}_i) = \frac{1}{N} \sum_{\mathbf{K}} e^{-i\mathbf{K} \cdot \mathbf{R}_i} \phi_{\mathbf{kK}}(\mathbf{r}) \]

The Bloch function is an eigenstate of the free electron part of the many body Hamiltonian

\[ \left[ \frac{p^2}{2m} + V(\mathbf{r}) \right] \phi_{\mathbf{kK}}(\mathbf{r}) = \epsilon_{\mathbf{kK}} \phi_{\mathbf{kK}}(\mathbf{r}) \]

Since this free electron Hamiltonian is invariant under space inversion
\[ \phi_{\alpha \kappa}(\vec{r}) = \phi_{\alpha \kappa}(-\vec{r}) \text{ within a phase factor.} \]

It is then straightforward to show that

\[ \phi_{\alpha}(\vec{r} - \vec{R}_1) = \phi_{\alpha}(-\vec{r} + \vec{R}_1) \text{ within a phase factor} \]

C.) Since the Hamiltonian appearing in the eigenvalue equation for the Bloch functions is real (in the non-relativistic case), its eigensolutions can all be chosen in the subspace of real functions. Since the Wannier functions form a complete set of states, they can then be also chosen to span the subspace of real functions. In this representation

\[ \phi_{\alpha}^*(\vec{r} - \vec{R}_1) = \phi_{\alpha}(\vec{r} - \vec{R}_1) \]

F.3) Electrical Energy

The electrical energy of an electron system in a uniform electric field \( E \) in the \( x \)-direction is:

\[ \mathcal{H}_E = -e x (\text{electric potential}) \]

\[ = e \sum_{i} \vec{r}_1 \cdot \vec{E} = e \sum_{i} \vec{x}_1 \cdot \vec{E} \]

where the sum extends over all the electrons.

The second quantization process gives

\[ \mathcal{H}_E = e E \int d\vec{r} \psi^*(\vec{r}) x \psi(\vec{r}) \]

which becomes after the expansion in Wannier states and the restriction to a single band model:
\[
\mathcal{H}_E = \sum_{ij} \delta \phi(\mathbf{r}-\mathbf{R}_i) \chi \phi(\mathbf{r}-\mathbf{R}_j) a_i^+ a_j^\sigma
\]

(Remember the Wannier functions can be chosen real.)

A.) If \( i = j \)

\[
M_{ij} = \int d\phi(\mathbf{r}-\mathbf{R}_i) \chi \phi(\mathbf{r}-\mathbf{R}_j)
\]

Writing \( \mathbf{r} = \mathbf{r} + \mathbf{R}_i \); \( \chi = \chi' + \chi_i \), \( d\mathbf{r} = d\mathbf{r}' \)

\[
M_{ij} = \int d\mathbf{r}' \phi(\mathbf{r}') \chi \phi(\mathbf{r}') + \chi_i \int d\mathbf{r}' \phi(\mathbf{r}') \phi(\mathbf{r}')
\]

where now \( \chi_i \) is the \( x \) component of the position of the \( i \) site.

The integrand in the first term is odd under space inversion and so the first integral vanishes. The second one equals \( \chi_i \) in view of the orthonormality of the Wannier functions.

\[
M_{ii} = \chi_i
\]

B.) If \( i \neq j \)

\[
M_{ij} = \int d\phi(\mathbf{r}-\mathbf{R}_i) \chi \phi(\mathbf{r}=-\mathbf{R}_j)
\]

Writing \( \mathbf{r} = \mathbf{r}' + \frac{\mathbf{R}_i + \mathbf{R}_j}{2} \); \( \chi = \chi' + \frac{\chi_i + \chi_j}{2} \); \( d\mathbf{r} = d\mathbf{r}' \)
\[ M_{ij} = \int dr' \phi(r') \frac{R_i - R_j}{2} x' \phi(r' + \frac{R_i - R_j}{2}) \]

\[ + \left( \frac{x_i + x_j}{2} \right) \int dr \phi(r-R_i) \phi(r-R_j) \]

The second term is zero because of the orthogonality of the Wannier functions. The integrand of the first term is odd under spatial inversion and so the first integral also vanishes.

\[ M_{ij} = 0 \]

Finally the electric energy is

\[ \mathcal{H}_E = e E \sum \sum x_i n_{i \sigma} \]

F.4) **Current Operator**

The classical definition of the current operator is

\[ J = -e \sum \mathbf{r}_{i} \]

or

\[ J = i e \sum [\mathbf{r}_{i}, \mathcal{H}_0] \]

The component of this current in the x direction is

\[ J_x = i e \sum [x_{i}, \mathcal{H}] \]
This is straightforwardly second quantized to be

\[ J_x = i e[\tilde{x}, \tilde{H}] \]

where \( \tilde{x} \) is the second quantized representation of \( x \) and \( \tilde{H} \), that of \( H \).

As seen in Section F.3.

\[ \tilde{x} = \sum_i \sum_{i\sigma} x_i n_{i\sigma} \]

\[ \tilde{H} = \sum_{ij} \sum_{i\sigma j\sigma} T_{ij} a_i^{\dagger} a_j + i \sum_i n_{i\uparrow} n_{i\downarrow} - \sum_i E_{n_i} \]

and so

\[ J_x = i e[\tilde{x}, \tilde{H}] \]

\[ J_x = \frac{ie}{2} \sum_{ij} \sum_{i\sigma j\sigma} (x_i - x_j) T_{ij} (a_{i\sigma}^{\dagger} a_{j\sigma} - a_{j\sigma}^{\dagger} a_{i\sigma}) \]
APPENDIX G

High Temperature Thermodynamics

Let us consider a general Hamiltonian $H = H_0 + H_1$

where $H_0$ conserves particles at every site

$$[n_{i0}, H_0] = 0$$

while $H_1$ does not (all parts of $H_1$ which conserve particles have been removed from $H_1$)

$$[n_{i0}, H_1] \neq 0$$

A.) The density operator is then

$$e^{-\beta H} = e^{-\beta(H_0 + H_1)}$$

$$= e^{-\beta H_0} \{ 1 - \int_0^\beta dt e^{H_0 t} H_1 e^{-H_0 t} + \ldots \}$$

using the expansion in Equation (4.2). In the limit $\beta \to 0$ the terms omitted in the above expansion can be forgotten to order $\beta$, since they involve higher powers of $\beta$.

To show this, let us look at such a term in the expansion ($n \geq 2$)

$$\int_0^\beta \int_0^{\tau_1} \int_0^{\tau_2} \ldots \int_0^{\tau_{n-1}} d\tau_1 d\tau_2 \ldots d\tau_n H_1(\tau_1) H_1(\tau_2) \ldots H_1(\tau_n)$$

where $H_1(\tau_1) = e^{H_0 \tau_1} H_1 e^{-H_0 \tau_1}$
Since $\beta \to 0$, this implies all integration variables $\tau_1 \ldots \tau_n$ will be less or equal to $\beta$. Thus to lowest order in $\beta$, such a term is

$$\int_0^\beta \int_0^{\tau_1} \int_0^{\tau_2} \ldots \int_0^{\tau_{n-1}} \left( \mathcal{H}_0(0) \mathcal{H}_1(0) \ldots \mathcal{H}_1(0) \right) d\tau_1 d\tau_2 \ldots d\tau_n$$

$$= \frac{\beta^n}{n!} \mathcal{H}_1^n(0)$$

Q.E.D.

B.) As was mentioned in Section III.1, it is easily shown that the thermodynamic average of any operator $\Theta$ is to order $\beta$: 

$$\langle \Theta \rangle = \langle \Theta \rangle_0 + \int_0^\beta d\tau \langle \mathcal{H}_0 \mathcal{H}_1 e^{(\Theta-\langle \Theta \rangle_0)} \rangle_0$$

where the averages $\langle \rangle_0$ are performed in the representation of $\mathcal{H}_0$.

Since $\mathcal{H}_0$ conserves particles at each site, this automatically implies the eigenstate of $\mathcal{H}_0$ also are eigenstates of the site number operators. Thus if $\Theta$ is an operator which also conserves particles at a site (such as $n_{i+}, n_{i+}^*, (n_{i+} - n_{i+}^*)$, and since $\mathcal{H}_1$ is strictly off-diagonal in the number representation, this means

$$\langle \mathcal{H}_1 e^{(\Theta-\langle \Theta \rangle_0)} \rangle_0 \equiv 0$$

Thus to order $\beta$, the thermodynamic average at high temperatures of an operator $\Theta$ satisfying $[n_{i+}, \Theta] = 0$ is independent of any particle non-conserving terms in the Hamiltonian.
APPENDIX H

Conductivity for a Lossy System

Kubo's(11) expression for the conductivity is

\[ \sigma(\omega) = \lim_{\varepsilon \to 0^+} \int \frac{\beta}{\omega} \int d\lambda \int d\nu e^{-(i\omega+\varepsilon)\nu} \langle J_x(-i\lambda)J_x(\nu) \rangle \]

The general time dependence of the current on a time dependent electric field \( E(t) \) will then be, according to Kubo:

\[ J_x(t) = \frac{1}{2\pi} \int_{-\infty}^{t} dt' \int_{-\infty}^{\infty} d\omega e^{i\omega(t-t')} \sigma(\omega)E(t') \]

\[ = \lim_{\varepsilon \to 0^+} \int_{-\infty}^{t} dt' \int \frac{\beta}{\omega} e^{-\varepsilon(t-t')} \langle J_x(-i\lambda)J_x(t-t') \rangle E(t') \]

But then statistical mechanics says that collisions which cause losses in the system are characterized by a relaxation time \( \tau \) such that once an electric field is turned off, the current will relax in the following way:

\[ \frac{\partial J_x(t)}{\partial t} = \frac{J_x(t)}{\tau} \]

Since we are dealing with complex currents, this relaxation relation can be rewritten

\[ \frac{\partial |J_x(t)|^2}{\partial t} = -2 \frac{|J_x(t)|^2}{\tau} \]

* This relation is easily deduced from the analysis in Reif (34), Section 14.6, or Wang (35), Section 4.1.
In the Kubo formalism, once the electric field has been turned off
\[ \frac{\partial |J_x(t)|^2}{\partial t} = \lim_{\varepsilon \to 0^+} -2\varepsilon \int dt' \int d\lambda e^{-\varepsilon(t-t')} \langle J_x(-i\lambda)J_x(t-t')|E(t') \rangle^2 \]
\[ = 0 \]

This is typical of a lossless system, i.e., one with infinite relaxation time. It is easily seen that by lifting the requirement that $\varepsilon \to 0$ and treating $\varepsilon$ as a loss parameter, one would get
\[ \frac{\partial |J_x(t)|^2}{\partial t} = -2\varepsilon |J_x(t)|^2 \]
which is exactly of the required form for a lossy system with $\tau = 1/\varepsilon$.

One can then phenomenologically introduce losses in the Kubo formalism by simply considering $\varepsilon$ as a lossless parameter instead of in the limit $\varepsilon \to 0$.

\[ ^{+} \text{Note the time dependence in the } J_x J_x \text{ correlation term is purely imaginary. The absolute value of this term has no time dependence.} \]
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