THE THERMOELECTRIC PROPERTIES OF STRONGLY CORRELATED SYSTEMS

A Dissertation in
Physics
by
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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2008
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Abstract

Strongly correlated systems are among the most interesting and complicated systems in physics. Large Seebeck coefficients are found in some of these systems, which highlight the possibility for thermoelectric applications. In this thesis, we study the thermoelectric properties of these strongly correlated systems with various methods.

We derived analytic formulas for the resistivity and Seebeck coefficient of the periodic Anderson model based on the dynamic mean field theory. These formulas were possible as the self energy of the single impurity Anderson model could be given by an analytic ansatz derived from experiments and numerical calculations instead of complicated numerical calculations. The results show good agreement with the experimental data of rare-earth compound in a restricted temperature range. These formulas help to understand the properties of periodic Anderson model.

Based on the study of rare-earth compounds, we proposed a design for the thermoelectric meta-material. This manmade material is made of quantum dots linked by conducting linkers. The quantum dots act as the rare-earth atoms with heavier mass. We set up a model similar to the periodic Anderson model for this new material. The new model was studied with the perturbation theory for energy bands. The dynamic mean field theory with numerical renormalization group as the impurity solver was used to study the transport properties. With these studies, we confirmed the improved thermoelectric properties of the designed material.
# Table of Contents

List of Figures vii

List of Tables viii

Acknowledgments ix

Chapter 1

Introduction 1

1.1 Thermoelectricity and its applications 1

1.2 Heavy Fermion Metals 7

1.3 Thermoelectric meta-material 12

Chapter 2

The perturbation theory 19

2.1 Introduction 19

2.2 Description of the Model 21

2.3 Perturbation Theory in One Dimension 24

2.4 Higher Dimensions 29

2.5 Discussion 31

Chapter 3

The dynamic mean field theory 33

3.1 Introduction 33

3.2 Theory 35

3.3 Results 41

3.3.1 Spectral function 42

3.3.2 Optical conductivity 43

3.3.3 Seebeck coefficient 46
List of Figures

1.1 Setup for Seebeck effect ........................................... 1
1.2 A diagram of a solid state refrigerator. ......................... 5
1.3 The spectral function of $f$ electron. This spectra comes from num-
    erical renormalization group calculation. The sharp peak at zero
    frequency is the Kondo resonance. .............................. 9
1.4 Model in one dimension. (a) shows the structure of the quantum
    dot array. $l$ labels the $l$th unit cell. Other notations are explained in
    the text. (b) shows our assumptions of energy levels for the singlet
    state. The second electron in the quantum dot has an effective
    binding energy $E_f$, which is still much lower than the binding energy
    of conducting sites. This put the quantum dots in spin singlet
    states. We concentrate our study on this case in next chapter.
    Notations are explained in the text. ............................. 14
1.5 Square Lattice. The plot inside the rectangle is unit cell $(i, j)$ of
    the square lattice. $(i, j, 1)$ is the conducting site at the top of that
    unit cell. $(i, j, 2)$ is the conducting site at the right of that unit cell.
    Similar labelling is used for other unit cells. The unit cell $(i − 1, j)$
    and $(i, j − 1)$ are also shown in the plot. ...................... 15
3.1 The two dimensional version of the lattice considered in this study.
    The lattice we studied in this chapter is the infinite dimensional
    extension of it. ..................................................... 35
3.2 The on-site spectral function for the particle-hole symmetrical case.
    The black curve is for our model. The blue (gray) curve is for
    Hubbard model. The parameters are $t = 1; U = 4$. Unit for $\omega$ is $10t$. 41
3.3 The on-site spectral function for the particle-hole asymmetrical
    case. The inset is the imaginary part of hybridization function
    $\Delta(\omega)$. The parameters are $t = 1; U = 3; \epsilon_f = −2.5; \epsilon_c = −0.5$. Unit
    for $\omega$ is $5t$. .................................................. 42
3.4 The optical conductivity for the particle-hole symmetrical case. The black dots is for our model. The blue (gray) dots are for the Hubbard model. The parameters are $t = 1; U = 4$. Unit for $\omega$ is $10t$. 

3.5 The optical conductivity for the particle-hole asymmetrical case. The inset shows the same plot with y axis changed to log scale. The parameters are $t = 1; U = 3; \epsilon_f = -2; \epsilon_c = -0.5$. Unit for $\omega$ is $5t$. 

3.6 The transport distribution function for the particle-hole asymmetrical case. The $\delta = 0.0057U, 0.0056U, 0.0055U$ for red, blue and green plot respectively. The other parameters are $t = 1; U = 3; \epsilon_f = -2.5; \epsilon_c = -0.5$. Unit for $\omega$ is $5t$. 

4.1 The imaginary part of f electron’s self energy calculated by DMFT [58]. It is shown here that this part is proportional to $\sqrt{T}$. 

4.2 The $\frac{T}{S(T)\sigma(T)}$ are plot versus $\sqrt{T}$. The unit for $\frac{T}{S(T)\sigma(T)}$ is arbitrary. The data in the bottom plot comes from DMFT calculation[58]. The experiment data are from refs. [80, 81, 82, 83, 84]. 

4.3 The magnetic susceptibility of SIAM is fitted with the formulas for the density of states of Kondo liquid. The $T_0$ is around $8T_K$ in the fitting.
List of Tables

1.1 Seebeck coefficients for selected heavy Fermion metals. $S$ is the Seebeck coefficient. $\rho$ is the resistivity. PF is the power factor ($S^2/\rho$). The data of a good semiconductor thermoelectric $Bi_2Te_3$ is shown for comparison. Data were taken from ref.[3]. 

7
Acknowledgments

I would like to express my deepest gratitude to my advisor Prof. Gerald Mahan. It is a privilege to have had him as my thesis advisor. I enjoy working on the research topics he has recommended. His guide, support and encouragement are invaluable. It is him who made all these works possible. I really appreciate all these.

I would like to thank Prof. Jainendra Jain. I appreciate his comments in the joint journal club and his suggestion in various problems. I also would like to acknowledge the help of other members in my thesis committee, Prof. Jorge Sofo and Prof. John Badding. They have helped me in various ways.

I am also grateful to my friends in Penn State, Jie Li, Qiujie Lv and Longhua Jian. They help me in my research and make my stay at Penn State enjoyable. I am forever indebted to my family. Their understanding and support mean everything to me.
Dedication

To My Family.
Introduction

1.1 Thermoelectricity and its applications

Thermoelectricity is a transport phenomenon. It refers collectively to the Seebeck effect, the Peltier effect and the Thomson effect. The Seebeck effect was discovered first by Thomas Seebeck in 1823. This effect refers to the generation of a voltage $V$ in an open circuit, as shown in fig 1.1. The circuit is made up of two different materials. The junctions, which are the interfaces between two different materials, are kept at different temperature $T_1, T_2$. Based on this phenomena, the Seebeck

Figure 1.1. Setup for Seebeck effect
coefficient $S$ is defined as\[1\]:
\[
S = \frac{V}{T_1 - T_2}
\]
(1.1)

The junctions do not contribute to the voltage generation. The voltage difference is in proportion to the difference of electrochemical potential. But at a particular temperature, the entire junction has the same electrochemical potential. So there is no voltage difference across the ends of a junction. Based on this argument, the Seebeck coefficient is considered as a property of a particular material. The contact to any other materials and the junctions are not necessary in the definitions. We notice that there is another popular definition of Seebeck coefficient\[2, 3, 4, 5, 6\], which is defined as the coefficient for effective electric field generated by temperature gradient.
\[
S' = \frac{E}{\nabla T}
\]
(1.2)

This definition is preferred by theorists. So we call it the theoretical Seebeck coefficient. While we refer to previous one as the phenomenal Seebeck coefficient. We noticed that the theoretical Seebeck coefficient is not equivalent to the phenomenal one. The relationship between the theoretical Seebeck coefficient and phenomenal one was studied by us\[7\]. It was shown that the theoretical Seebeck coefficient is a universal constant for homogeneous doped semiconductor, while the phenomenal Seebeck coefficient decreases with the logarithm of the density of the carriers. Based on this result, for a homogeneous doped semiconductors, the electric field induced by temperature gradient is a constant independent of materials. The detail of this study is given in appendix A.

If the circuit in fig 1.1 was closed and a current was carried in the circuit, the current would carry heat from one junction to the other. This is the Peltier effect. The heat current $J_{Qp}$ caused by the charge current in this effect is proportional to
the charge current $\vec{J}$:

$$\vec{J}_{qp} = \Pi \vec{J}$$  \hspace{1cm} (1.3)$$

where $\Pi$ is the Peltier coefficient. Another contribution to the heat current comes from the temperature gradient. So the total heat current $\vec{J}_Q$ is given by:

$$\vec{J}_Q = \Pi \vec{J} - K \nabla_r T$$  \hspace{1cm} (1.4)$$

where $K$ is the thermal conductivity. The charge current in this circuit is given by:

$$\vec{J} = \sigma \vec{E} - \sigma S \nabla_r T$$  \hspace{1cm} (1.5)$$

where $\sigma$ is the electrical conductivity, $\vec{E}$ is the electric field.

In 1854, William Thomson (Lord Kelvin) noticed that there should be a thermodynamical connection between the Peltier effect and the Seebeck effect. He found that the Seebeck coefficient is related with the Peltier coefficient by:

$$S = \Pi / T$$  \hspace{1cm} (1.6)$$

This is one of the Onsagers reciprocity relations. Based on this study, he also predicted a third effect, which is named after him as the Thomson effect. The Thomson effect is the cooling or heating of a current-carrying conductor with
Seebeck coefficient gradient. The heat production at the conductor is given by:

\[ Q' = -\nabla_r \tilde{J}_p = -\tilde{J} \nabla_r S \]  \hspace{1cm} (1.7)

where \( Q' \) is the heat production in the conductor. The Thomson effect can be considered as a combination of Seebeck effect and Peltier effect.

Most conductors have a small Seebeck coefficient. They can be used to make thermocouples, which could be devices for temperature measurement. In 1950s, Abram Ioffe found that doped semiconductors had a much larger thermoelectric effect than did other materials. He proposed that thermoelectric effects can be used to make solid state refrigerators[8]. Such refrigerator is made of two thermal reservoirs with thermoelectric materials sandwiched between them, as shown in fig.1.2. This device makes use of the Peltier effect. The heat is transferred from the cold reservoir to the hot reservoir by a current caused by external voltage. Such refrigerators have no moving parts, which make them very reliable. They are also environmental friendly compared to refrigerators based on Freon compressor. However the solid state refrigerators made of the best semiconductor thermoelectric materials have only about one-third of the efficiency of the Freon technology[3].

The proposal for research in the thermoelectric is to develop new materials, which improve the efficiency of the refrigerators. The main topic of this thesis is to show how strongly correlated systems can be engineered to achieve better efficiency for the refrigerators and why such good efficiency can be achieved.

We show briefly how the efficiency of the refrigerators depend on the properties of the thermoelectric materials. Some further discuss can be found in the appendix.

A. We consider a bar with length \( L \) and unit cross section made of certain homogeneous thermoelectric material. One end of the bar is kept at temperature \( T_c \).
Figure 1.2. A diagram of a solid state refrigerator.

The other end is kept at higher temperature $T_h$. In this one dimensional geometry, we can solve following Dominical’s equation for the conservation of energy to find the temperature distribution of the bar[3],

$$\frac{J^2}{\sigma} + K \nabla^2 T = 0. \quad (1.8)$$

The temperature distribution is found to be:

$$T(x) = T_c + \frac{x}{T}(T_h - T_c) + \frac{J^2}{2\sigma K} x(L - x) \quad (1.9)$$

where $x$ is the position. The origin is at the cold end of the bar. Based on equation (1.4), the rate of the heat removed from the cold end is given by:

$$J_Q(T_c) = SJT(0) - K \nabla T(x)|_{x=0}$$
The input power is given by:

\[ P = J \left[ \frac{J L}{\sigma} + S(T_h - T_c) \right] \]  

(1.11)

So the efficiency is:

\[ \eta(J) = \frac{J_Q(T_c)}{P} = \frac{ST_cJ - K \Delta T/L - J^2L/(2\sigma)}{J^2L/\sigma + SJ\Delta T} \]  

(1.12)

The efficiency depends on the input current. We can maximize the efficiency by varying the current \( J \). The maximum efficiency is called the coefficient of performance (COP) and is given by:

\[ \text{COP} = \frac{T_c \gamma - T_h}{(T_h - T_c)(\gamma + 1)} \]  

(1.13)

\[ \gamma = \sqrt{1 + Z(T_h + T_c)/2} \]  

(1.14)

\[ Z = \frac{\sigma S^2}{K} \]  

(1.15)

where \( Z \) is the key parameter of a material related to thermoelectric application and is called the figure of merit. Based on the above equations, the COP depends only on the figure of merit \( Z \). The efficiency of the device is increased by making \( Z \) as large as possible. All thermoelectric research is focused on finding materials with the highest value of \( Z \).
Table 1.1. Seebeck coefficients for selected heavy Fermion metals. \( S \) is the Seebeck coefficient. \( \rho \) is the resistivity. PF is the power factor \((S^2/\rho)\). The data of a good semiconductor thermoelectric \( \text{Bi}_2\text{Te}_3 \) is shown for comparison. Data were taken from ref.[3].

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T(K) )</th>
<th>( S(\mu V/K) )</th>
<th>( \rho(\mu \Omega \cdot \text{cm}) )</th>
<th>PF((\mu W/(K^2 \cdot \text{cm})))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Bi}_2\text{Te}_3 )</td>
<td>300</td>
<td>240</td>
<td>1700</td>
<td>35</td>
</tr>
<tr>
<td>( \text{CeAl}_3 )</td>
<td>50</td>
<td>42</td>
<td>115</td>
<td>15</td>
</tr>
<tr>
<td>( \text{CeCu}_6 )</td>
<td>40</td>
<td>52</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td>( \text{CePd}_3 )</td>
<td>140</td>
<td>125</td>
<td>170</td>
<td>92</td>
</tr>
<tr>
<td>( \text{YbPd} )</td>
<td>250</td>
<td>-104</td>
<td>145</td>
<td>75</td>
</tr>
<tr>
<td>( \text{YbAl}_3 )</td>
<td>300</td>
<td>-90</td>
<td>45</td>
<td>180</td>
</tr>
</tbody>
</table>

1.2 Heavy Fermion Metals

The most important thermoelectric materials currently available are semiconductors [3]. Large number of new complex materials are under investigation for future thermoelectric applications[8]. Heavy Fermion metals are among these materials. Large Seebeck coefficients are found in some heavy Fermion metals, as shown in table 1.1.

Heavy Fermion metals are alloys that show Fermi-liquid behavior at low temperature with very large effective mass compared to ordinary metals. The mass enhancement is seen in properties such as paramagnetic susceptibility, heat capacity and resistivity[9]. The constituents of these materials include rare-earth or actinide atoms, which have partially filled \( 4f \) or \( 5f \) electron shells. These \( f \) electrons are highly localized. There is a strong repulsive Coulomb interaction between electrons on the same atom, which is the on-site correlation. The localization of the \( f \) electrons causes the on-site correlation to be essential in the models. The \( f \) electrons are expected to move so as not to approach each other to reduce the Coulomb energy in such models. The above correlation of electrons
due to Coulomb interaction is called "electron correlation"[10, 11]. The energy associated with the electron correlation is named the correlation energy. Besides the correlation energy, the electrons also have kinetic energy and Hartree-Fock energy, which can be found with the Hartree-Fock approximation. So in other word, the correlation of electrons beyond the Hartree-Fock approximation is the electron correlation. Systems in which electron correlation plays an important role are called strong correlated systems. Heavy Fermion metal belongs to the strong correlated systems. For such systems, theory beyond Hartree-Fock approximation should be used.

The large Seebeck coefficient of the heavy Fermion metal is caused by the $f$ electrons. One standard model of on-site correlation for discussing the properties of these heavy Fermion metals is the single impurity Anderson model[12, 13]. The model is given by following Hamiltonian:

$$H = \sum_{k,\sigma} [\epsilon_k C_{k\sigma}^\dagger C_{k\sigma} + \frac{1}{\sqrt{N}} (VC_{k\sigma}^\dagger f_\sigma + h.c)] + \sum_{\sigma} \epsilon_f f_{\sigma}^\dagger f_{\sigma} + U n_{\uparrow}^f n_{\downarrow}^f \quad (1.16)$$

$$n_{\sigma}^f = f_{\sigma}^\dagger f_{\sigma} \quad (1.17)$$

Where $f_{\sigma}(f_{\sigma}^\dagger)$ destroys (creates) a correlated $f$ electron with spin $\sigma$ and energy $\epsilon_f$. Similarly, $C_{k\sigma}(C_{k\sigma}^\dagger)$ destroys (creates) a conduction $s$-$d$ electron with wave vector $k$, spin $\sigma$ and energy $\epsilon_k$. The $f$ electrons hybridize with the conduction electrons via the matrix element $V$. $N$ is the number of atom sites in the solid. $U$ denotes the Coulomb interaction between two $f$ electrons at the same site, which describes the on-site correlation. Simple as the Hamiltonian, this model is very difficult to solve. Many methods have been applied to this model. These methods include Bethe ansatz[14, 15], perturbation theory[16, 17, 18, 19], equa-
Figure 1.3. The spectral function of $f$ electron. This spectra comes from numerical renormalization group calculation. The sharp peak at zero frequency is the Kondo resonance.

The most important feature in the solutions to the single impurity Anderson model is the presence of the Kondo resonance at temperature lower than the Kondo temperature $T_K$. The Kondo resonance is a sharp peak near the chemical potential in the spectral function of the $f$ electron $A_f(\omega)$. This resonance results from a dynamical spin-flip process. Most theories determine the Kondo resonance numerically. A typical Kondo resonance is shown in Fig.1.3. An analytical result for the shape of the Kondo resonance is still not available. Some general properties are known, which helps to get a qualitatively understanding of the properties of the model.

1. The Kondo resonance is scaled. For a given $\eta(= 1 + 2\epsilon_f/U)$, the Kondo
resonance is scaled by a single parameter proportional to Kondo temperature $T_K[25]$.

2. The $f$ electron’s spectral function $A_f(\omega)$ should be approximated by a Lorenz function at frequency very close to the chemical potential ($|\omega| \ll k_B T$, $k_B$ is the Boltzmann constant). Because at temperature much lower than the Kondo temperature, the system is a Fermi-liquid.

3. The Kondo resonance is not a Lorenz peak[22]. The tail of the Kondo resonance is given by[25]:

$$
\pi \Delta_0 D(\omega) = \frac{1}{2} \left[ \frac{1}{(\frac{1}{\pi} g_+ \ln |\omega'|)^2 + 1} + \frac{1 + 4g_-}{(\frac{1}{\pi} g_- \ln |\omega'|)^2 + 1 + 4g_-} \right]
$$

$$
\omega' = \alpha \frac{\omega}{k_B T_K}, g_\pm = \beta/(1 \pm \eta), \eta = 1 + \frac{2\epsilon_f}{U}
$$

where $\alpha$ and $\beta$ are two constants.

The conductivity and Seebeck coefficient for single impurity Anderson model are given by[12]:

$$
\frac{1}{\tau(\omega)} = \frac{1}{\tau_0(\omega)} + cu A_f(\omega)
$$

$$
\sigma(T) = \frac{e^2}{\hbar a} \int_{-\infty}^{\infty} [-f'(\omega)] g(\omega) \tau(\omega) d\omega
$$

$$
S(T) = \frac{1}{T \sigma \hbar a} \int_{-\infty}^{\infty} [-f'(\omega)] (\omega - \mu) g(\omega) \tau(\omega) d\omega
$$

where $\tau$ is the relaxation time. $\tau_0$ is the relaxation due to non-magnetic impurity and phonon scattering. $c$ is the concentration of the rare-earth atoms. $u$ is another constant. $a$ is the lattice constant. $f(\omega)$ is the Fermi distribution function. $g(\omega)$ is the density of state of the conduction band. We assume $\tau_0$ is small and can be
neglected. Then based on above formulas, the Seebeck coefficient is given by:

\[ S \propto \tau'(\mu)/\tau(\mu) = -A_f(\mu)'/A_f(\mu) \]  

(1.23)

The Kondo resonance leads to a large value of \( A_f(\mu)'/A_f(\mu) \), which leads to the large Seebeck coefficient for heavy Fermion metals.

The single impurity Anderson model is able to explain some properties of the heavy Fermion metals, such as large Seebeck coefficients, while it completely ignores the interaction between \( f \) electrons and the coherence of \( f \) electrons. The interaction between \( f \) electrons is key for the magnetic properties of the rare-earth compound. The coherence of \( f \) electrons is important for the transport properties. To described the interactions and coherence of the \( f \) electrons at different atom sites, another standard model is introduced, which is the periodic Anderson model. The model is given by following Hamiltonian.

\[
H = \sum_{k,\sigma} [\epsilon_k C_{k\sigma}^\dagger C_{k\sigma} + (V C_{k\sigma}^\dagger f_{k\sigma} + h.c)] + \sum_{\mathbf{i},\sigma} (\epsilon_f f_{\mathbf{i}\sigma}^\dagger f_{\mathbf{i}\sigma} + \frac{U}{2} n_{\mathbf{i}\sigma} n_{\mathbf{i}-\sigma}^f) \]  

(1.24)

where \( f_{k\sigma} \) is the Fourier transform of \( f_{\mathbf{i}\sigma} \). Other notations are the same as those in the single impurity Anderson model. The solution to the periodic Anderson model is much more difficult than the single impurity Anderson model. The analytic solution is still a main challenge in condensed matter theory. The Bethe ansatz can not be applied to this model. Many methods developed for single impurity Anderson model have been applied to the periodic model with certain modifications. Most results depend heavily on numerical calculations\[21, 39, 40, 41, 42, 43, 44, 45\]. The theories show considerable agreement with the experiments.

The dynamic mean field theory is the most popular theory currently. This theory
transfer the periodic model into an effective single impurity model by treating the media surrounding an interacting site as a self-consistent mean field. The methods developed for single impurity model can be applied to solve the effective single impurity model. The success of dynamic mean field theory in describing the properties of $V_2O_3$ is a milestone for this theory[46]. The dynamical mean field theory provides a lot insight into this model. Part of this thesis is based on dynamic mean field theory. The detail of the dynamical mean field theory is provide in appendix B.

Similar to the spectral function $A_f(\omega)$, the self energy $\Sigma_\sigma(\omega)$ of the single impurity model has some well defined properties. This includes:

1. $Im\Sigma_f(\mu) = 0$.

2. $Im\Sigma_f(\omega) \propto (\omega - \mu)^2$ as $\omega \to \mu$

3. $Im\Sigma_f(\omega) \propto T^{1/2}$ where $T$ is the temperature.

These properties of the single impurity model can be combined with dynamic mean field theory to obtain some further insights to the heavy Fermion metals. In this way, we derived some analytic formulas for the resistivity and Seebeck coefficient for the periodic Anderson model. The formulas show good agreement with the experiments of rare-earth compounds and give a better explanation for the large Seebeck coefficient of the heavy Fermion metals. The detail of this study is given in chapter 4 of this thesis.

1.3 Thermoelectric meta-material

Based on the study of heavy Fermion metals, we are convinced that strong correlation is possible to improve the efficiency of solid state refrigerators. As shown
in table 1.1, heavy Fermion metals can achieve higher power factor $\sigma S^2$ than the best semiconductor thermoelectric material $Bi_2Te_3$. While heavy Fermion metals also have large thermal conductivity due to electrons, which limits their applications. Reducing the thermal conductivity is another key in improving the efficiency of thermoelectric applications. With the advance in modern fabrication, we now can design new complex materials for particular application. Such materials are called meta-material. The most well known meta-materials are electromagnetic meta-materials, which are designed for optical and microwave applications. Based on our knowledge of thermoelectricity and heavy Fermion metal, we can design thermoelectric meta-materials.

The design we proposed is the crystalline arrays of quantum dots connected by conducting chains of linkers. The structures of these materials in one and two dimension are shown in fig. 1.4 and fig. 1.5 respectively. The quantum dots are periodic clusters of atoms. These quantum dots have the strong on-site correlation as the rare-earth atoms[30, 31, 32, 33, 34, 35, 36]. They can also be successfully described as Anderson impurities in the single impurity Anderson model[28, 37, 38]. Similar to the heavy Fermion metals, the strong correlation is expected to lead to the large Seebeck coefficients in this material. The linkers are conducting atoms or molecules. The electrical conductivity is expected to be improved due to these conducting linkers. Overall, the energy band of this new material is possible to be tuned relative easily by the structure and the components and made suitable for thermoelectric applications. Further more, low thermal conductivity can be expected due to the heavy mass of quantum dots. These properties add up to a large value of the figure of merit, which give the material the potential for thermoelectric application.

We setup a model to describe above thermoelectric meta-material. Electrons in
Figure 1.4. Model in one dimension. (a) shows the structure of the quantum dot array. $l$ labels the $l$th unit cell. Other notations are explained in the text. (b) shows our assumptions of energy levels for the singlet state. The second electron in the quantum dot has an effective binding energy $E_f$, which is still much lower than the binding energy of conducting sites. This puts the quantum dots in spin singlet states. We concentrate our study on this case in next chapter. Notations are explained in the text.

the conducting sites are described by a tight binding model with transfer term $W$. Quantum dots are treated as Anderson impurities as explained. The Hamiltonian depends on the dimension considered. The Hamiltonian in one dimension (1D) is given by:

$$H = E_0 \sum_{l,\sigma} C_{l,l,\sigma}^+ C_{l,l,\sigma} + W \sum_{l,\sigma} (\sum_{j=1}^{N-1} C_{l+1,j,\sigma}^+ C_{l,j,\sigma} + \text{h.c.})$$

$$+ \sum_l (\sum_{\sigma} \varepsilon_f n_{l,\sigma} + n_{l\uparrow} n_{l\downarrow} U) + V \sum_{l,\sigma} [f_{l,\sigma}^+ (C_{l+1,1,\sigma} + C_{l,N,\sigma}) + \text{h.c.}]$$

$$n_{l,\sigma} = f_{l,\sigma}^+ f_{l,\sigma}$$

(1.25)
Figure 1.5. Square Lattice. The plot inside the rectangle is unit cell \((i, j)\) of the square lattice. \((i, j, 1)\) is the conducting site at the top of that unit cell. \((i, j, 2)\) is the conducting site at the right of that unit cell. Similar labelling is used for other unit cells. The unit cell \((i−1, j)\) and \((i, j−1)\) are also shown in the plot.

where \(l = 1\) to \(n\) labels the period, \(j = 1\) to \(N\) labels the sites along the conducting chain, and \(\sigma\) labels the spin. \(C_{l, i, \sigma}\) is the destruction operator for electron with spin \(\sigma\), binding energy \(E_0\) at conducting site \((l, i)\). \(f_{l, \sigma}\) is the destruction operator for electron with spin \(\sigma\), binding energy \(\epsilon_f\) at quantum dot site \(l\). \(U\) is the Coulomb interaction as usual. Higher dimension Hamiltonian is shown in chapter.2.

This theoretical model can be considered as an extension of the Hubbard model by adding to it non-interacting linker sites. This extension makes our model very different from the Hubbard model. The exchange interaction between two neighboring correlated sites in the Hubbard model is replaced by super-exchange in our model. This results in different magnetic properties for our model, which may be the topic for future study. Another obvious difference is the metal-insulator transition, which appears in both the Hubbard model and the periodic Anderson
model[49], does not appear in our model as shown in chapter.3. In that chapter, we will show that this new model also has improved conductivity and Seebeck coefficient compared to Hubbard model.

It is worth while to compare this new model with the periodic Anderson Model discussed in previous section. In the periodic Anderson model, the correlated electrons are an alternate channel for the conducting electrons. The conducting electrons have a self-energy term which is usually called something like

\[
\Delta(\omega) = V^2 \sum_k \frac{1}{E - E(k) + i\eta} \tag{1.27}
\]

The imaginary part of this self-energy is \( \Delta_2 = -\pi V^2 \rho(E) \), where \( \rho(E) \) is the density of states. This damping term imparts the energy width to the various electron energy states. Our model does not have this term. The correlated states are not in a side channel, but are blocking the main channel. This makes the physics of our model very different than found in the usual periodic Anderson model.

The energy states of electrons that can move through the crystal are of fundamental interest. The knowledge of energy band is useful in understanding the properties of the materials. We study the energy band with the perturbation theory[47]. The on-site correlation is treated as a perturbation. Such perturbation theory only works when the Coulomb interaction \( U \) is small in the model we are considering. But as the perturbation theory for the single impurity model, this theory still provides valuable insights into the physics of the model. This study of energy band with perturbation theory is the main topic in the next chapter. Unfortunately, the summations of the Feynman diagrams in the second order perturbation theory in the general case are way too complicated. For simplicity, the spin singlet state for quantum dots is assumed. Then each quantum dot is in the same quantum state,
except for fluctuations, which does result in energy bands. Other ground state spin configurations for the quantum dot are the subject of future studies. With this assumption, the spin of conducting electron is irrelevant. And the ground state for quantum dots is determined. The energy band is found to depend on the number of conducting linkers between quantum dots $N$, the coupling between linkers and quantum dots $V$ and the interaction inside the quantum dots $U$. This result indicts we have many choice to design the energy band of the material for application, which doesn’t happen to most materials. The Kondo resonance is not present in this case. The transport properties should be similar to ordinary metal, which is not interesting to us.

It is difficult to extend the perturbation theory to the general cases. We continue our study of the thermoelectric meta-material with the dynamic mean field theory[48]. This dynamic mean field theory for the thermoelectric meta-material is the subject of chapter.3. In this theory, the lattice model is mapped self-consistently into an effective single impurity Anderson model. The effective single impurity Anderson model is then solved with the numerical reorganization group developed by Wilson et. al. Transport properties such as Seebeck coefficient and optical conductivity are evaluated with Kubo formulas. The theory provides the exact solution only for the model in infinite dimension, as shown in appendix.B. It has been shown that the three dimension correlation functions can be approximated by the corresponding correlation functions in the mode of infinite dimension[50]. The experiments also agree with calculations based on models of infinite dimensions[51]. Based on these facts, we believe the dynamic mean field theory gives the properties for the real materials. The Kondo resonance is found in the spectral function of electrons on the quantum dots. High Seebeck coefficients (> $100\mu V/K$) with good conductivity are obtained for proper parameter setups.
The calculations confirmed our design for the thermoelectric meta-material.
The perturbation theory

2.1 Introduction

Modern fabrication techniques permit the growth of many new materials. Of present interest are crystalline arrays of quantum dots connected by conducting chains of linker atoms[52, 53, 54, 55]. The linkers are conducting atoms or molecules. The quantum dots are clusters of atoms, or a molecule. Figure 1.4 shows a possible arrangement of such a material. The energy bands of these new crystals can be tuned by the structure, and should have many industrial uses. They are expected to have large electrical conductivity due to the conducting atoms, low thermal conductivity due to the heavy mass of quantum dots, and high thermoelectric coefficient due to the high density of states near the chemical potential.[57] These properties add up to a large value of the figure of merit, which is essential for application in solid state refrigerators. They can also be single electron transistors[28], or good optical materials. In optical physics they are called metamaterials, but this name has not caught-on in other fields. The experimental
study of such materials is underway[55].

In order to calculate the properties of such materials, we need to know the energy states of electrons that can move through the crystal. There have been several calculations of band structures of quantum dot crystals[29]. They have treated the states of the quantum dot as an one-electron problem, while ignoring any correlation. On the other hand, many other calculations note that electron transmission through a quantum dot is a problem with strong correlation[30, 31, 32, 33, 34, 35, 36]. Here we calculate the energy bands of conducting electrons through these metamaterials, while treating the quantum dots as a strongly correlated system. Every quantum dot is treated as an Anderson impurity as in the periodic Anderson model (PAM)[28, 37, 38].

We convinced ourselves that an exact solution, in one dimension, using the Bethe Ansatz, is not possible. So we have proceeded to use a perturbation method. Our method is first described in detail in one dimension, and then easily expanded to two and three dimensions. For simplicity, the spin singlet state for quantum dots is assumed. Then each quantum dot is in the same quantum state, except for fluctuations, which does result in energy bands. Other ground state spin configurations for the quantum dot are the subject of future studies. With this assumption, the ground state for quantum dots is determined, and the spin of conducting electron is irrelevant. The energy band is found to depend on the number of conducting linkers between the quantum dots $N$, the coupling between linkers and quantum dots $V$, and the interaction inside of the quantum dot $U$.

This chapter is organized as follows. The model for one dimensional (1D) quantum dot arrays is described in Section 2.2. The energy bands in 1D are solved in Section 2.3. Higher dimensions are discussed in Section 2.4. Conclusions are presented in Section 2.5.
2.2 Description of the Model

The energy bands are first solved in one dimension. Figure 1.4 illustrates the basic geometry. We consider a chain of atoms with \( n \) unit cells. Every unit cell has \( N \) conducting sites and one correlated site. Electrons in the conducting sites are described by a tight binding model with transfer term \( W \).

We assume the ground state is a spin singlet of two electrons. They are denoted as \( f \)-electrons, in agreement with the vast literature on heavy fermions. The choice of spin singlet means that every correlated site has the same ground state, and there is no need to worry about magnetic ordering. We restrict our calculation to a restricted Hilbert space, in which every correlated site can have one, two, or three such \( f \)-electrons. Periodic boundary condition is also applied.

The Hamiltonian is:

\[
H = E_0 \sum_{l,j,s} C_{l,j,s}^\dagger C_{l,j,s} + W \sum_{l,s} \left( \sum_{j=1}^{N-1} C_{l,j+1,s}^\dagger C_{l,j,s} + \text{h.c.} \right) + \sum_l \left( \varepsilon_f \sum_s n_{l,s} + n_{l\uparrow} n_{l\downarrow} U \right) + V \sum_{l,s} [f_{l,s}^\dagger (C_{l+1,1,s} + C_{l,N,s}) + \text{h.c.}] 
\]

\[
n_{l,s} = f_{l,s}^\dagger f_{l,s}
\]

where \( l = 1 \) to \( n \) labels the period, \( j = 1 \) to \( N \) labels the sites along the conducting chain, and \( s \) labels the spin. \( C_{l,i,s} \) is the destruction operator for electron with spin \( s \) at conducting sites \((l, i)\). \( E_0 \) is the binding energy for the conducting electrons. With a wave vector transform,[56] we can diagonalize the conducting chain in each period:
\[ \phi_j(\alpha) = \sqrt{\frac{2}{N+1}} \sin(k_{\alpha j}), \quad k_{\alpha} = \frac{\pi \alpha}{N+1} \]  

(2.3)

where \( j \) labels the conducting site locations, ranging from 1 to \( N \), \( \alpha \) labels the wave vectors, ranging from 1 to \( N \).

\[ C_{l,j,s} = \sum_{\alpha=1}^{N} C_{l,\alpha,s} \phi_j(\alpha) \]  

(2.4)

\[ C_{l,\alpha,s} = \sum_{j=1}^{N} C_{l,j,s} \phi_j(\alpha) \]  

(2.5)

\[ H = \sum_{\alpha,l,s} \varepsilon_{\alpha} C_{l,\alpha,s}^\dagger C_{l,\alpha,s} + \sum_{l} \{ \sum_{s} \varepsilon_f n_l,s + n_{l\uparrow} n_{l\downarrow} U \} + V \sum_{l,\alpha,s} \{ f_{l,s}^\dagger [C_{l+1,\alpha,s} \phi_1(\alpha) + C_{l,\alpha,s} \phi_N(\alpha)] + h.c. \} \]  

(2.6)

\[ \epsilon_{\alpha} = E_0 + 2W \cos(k_{\alpha}) \]  

(2.7)

Typically the quantum dots are connected by short molecules, so that \( N \) is a small integer such as 1, 2, or 3. Then the conducting electrons do not form a continuous band in energy states, between the dots, but have a few discrete energy values.

Our strategy for solving for the energy bands is to effectively replace the correlated site by a \( T \)-matrix. To order \( O(V^2) \) it can be replaced by a term in the Hamiltonian which connects conducting sites on each side of it

\[ H_T = \sum_{l,\alpha,\beta,s} T_{l,\alpha;l+1,\beta} C_{l,\alpha,s}^\dagger C_{l+1,\beta,s} + h.c. \]  

(2.8)

\[ T_{l,\alpha;l+1,\beta} = V^2 \phi_1(\beta) \phi_N(\alpha) G_f \]  

(2.9)
The correlated site has been replace by a term of the form $V^2 G_f$, where $G_f$ is the Green’s function of the correlated electrons. This type of replacement has been a standard mathematical trick since the early days of the Anderson model. The remaining question is: what is the form of $G_f$ for our model? That is the topic of the rest of this chapter. In our model, where the ground state of the correlated site is a spin singlet, then the transfer matrix is the same for each correlated site. Then we can omit the site labels, and call it $T_{\alpha,\beta}$. Once we introduce the transfer term $T_{l,\alpha;l+1,\beta}$, then it is easy to see that the conducting electrons have an energy band of the form

\begin{align*}
E(\alpha) &= \varepsilon_\alpha + 2T_{\alpha,\alpha} \cos(k) + \Sigma_\alpha \\
\Sigma_\alpha &= \sum_{\beta \neq \alpha} \frac{T_{\alpha,\beta}^2}{\varepsilon_\alpha - \varepsilon_\beta} + O(T^4)
\end{align*}

(2.10) (2.11)

where $k = \pi m/n$ is the wave vector of the periodic array of $n$-monomers. The wave vector $k$ creates a true energy band.

Every correlated site is assumed to have the energy levels shown in fig.1.4. The correlated site has two $f$-electrons in a spin singlet. The energy of the this dot is $2\varepsilon_f + U$ which we write as $E_G = 2E_f - U, E_f = \varepsilon_f + U$. The value of $E_G$ may, or may not, be similar to the energy of the linker chains $\varepsilon_\alpha = E_0 + 2W \cos(k_\alpha)$. The band width for the system is $V^2/(E_f - \varepsilon_\alpha)$ which we assume is small compared to $W$.

All of these assumptions are possible in real materials, but are chosen somewhat arbitrarily here. The intention is to keep the calculation simple. Later works may consider more complex arrangements of energy levels.
2.3 Perturbation Theory in One Dimension

The Hubbard term is treated as a perturbation, in the manner of references [43, 44]. The rest of the Hamiltonian is solved exactly. Such treatment is common for the Anderson model, and has proved to be useful [16, 17, 18, 19, 45], especially for the asymmetric Anderson model [18, 19].

We separate the Hamiltonian into two parts

\begin{align*}
H &= H_0 + V_h \quad (2.12) \\
H_0 &= \sum_{\ell} \left\{ E_f \sum_{s} n_{\ell,s} - U \langle n_{\ell,s} \rangle^2 + \sum_{\alpha,s} \varepsilon_{\alpha} C_{\ell,\alpha,s}^\dagger C_{\ell,\alpha,s} \right\} \quad (2.13) \\
&\quad + V \sum_{\ell,\alpha,s} \left\{ f_{\ell,s}^\dagger [C_{\ell,\alpha,s} \phi_1(\alpha) + C_{\ell-1,\alpha,s} \phi_{N}(\alpha)] + \text{h.c.} \right\} \quad (2.14) \\
E_f &= \varepsilon_f + U \langle n_{\ell,\uparrow} \rangle \quad (2.15) \\
V_h &= U \sum_{\ell} (n_{\ell,\uparrow} - \langle n_{\ell,s} \rangle)(n_{\ell,\downarrow} - \langle n_{\ell,s} \rangle) \quad (2.16)
\end{align*}

The notation is the same as in the prior section. $V_h$ is the perturbation. For a doubly occupied ground state,

\[ \langle n_{\ell,\uparrow} \rangle = \langle n_{\ell,\downarrow} \rangle \approx 1 \quad (2.17) \]

Introduce the lattice transform for the $n$ unit cells

\begin{align*}
f_{\ell,s} &= \frac{1}{\sqrt{n}} \sum_k f_{k,s} e^{ik\ell} \quad (2.18) \\
C_{\ell,\alpha,s} &= \frac{1}{\sqrt{n}} \sum_k C_{k,\alpha,s} e^{ik\ell} \quad (2.19)
\end{align*}
The Hamiltonian $H_0$ is now

$$
H_0 = \sum_k \{ E_f \sum_s n_{k,s} + \sum_{\alpha,s} \varepsilon_\alpha C_{k,\alpha,s}^\dagger C_{k,\alpha,s} \} - U \langle n_{f,s} \rangle^2 \\
+ \sum_{k,\alpha,s} [V_{k\alpha} f_{k,s}^\dagger C_{k,\alpha,s} + \text{h.c.}] \\
V_{k\alpha} = V[\phi_1(\alpha) + \phi_N(\alpha)e^{-ik}] = V\phi_1(\alpha)[1 - (-1)^\alpha e^{-ik}] \\
|V_{k\alpha}|^2 = 2V^2\phi_1^2(\alpha)[1 - (1)^\alpha \cos(k)] \\
n_{k,s} = f_{k,s}^\dagger f_{k,s}
$$

(2.20)

(2.21)

(2.22)

The factor of $\cos(k)$ in $|V_{k\alpha}|^2$ provides the basic dispersion of the electron energy bands. The exact Green’s function of the $f$-electrons is[10]

$$
G_f(k,\omega) = \frac{1}{\omega - E_f - \Sigma_f(k,\omega)} \\
\Sigma_f(k,\omega) = \sum_\alpha \frac{|V_{k\alpha}|^2}{\omega - \varepsilon_\alpha + i\eta}
$$

(2.24)

(2.25)

The $f$-electron Green’s function has poles at the $N + 1$ solutions to

$$
E = E_f + \Sigma_f(E)
$$

(2.26)

An approximate solution has a $f$-electron pole at

$$
E_f(k) \approx E_f + \Sigma_f(E_f)
$$

(2.27)
Another exact way to write eqn.(2.26) is

\[ E = \varepsilon_\alpha + |V_{k\alpha}|^2 \tilde{G}_{f\alpha}(k, E) \]  

(2.28)

\[ \tilde{G}_{f\alpha}(k, E) = \frac{1}{E - E_f - \tilde{\Sigma}_{f\alpha}(E)} \]  

(2.29)

\[ \tilde{\Sigma}_{f\alpha}(k, E) = \sum_{\beta \neq \alpha} \frac{|V_{k\beta}|^2}{E - \varepsilon_\beta + i\eta} \]  

(2.30)

The Green’s function is

\[ G_\alpha(k, ik_n) = \frac{1}{ik_n - \varepsilon_\alpha - \Sigma_\alpha(k, ik_n)} \]  

(2.31)

\[ \Sigma_\alpha(k, ik_n) = |V_{k\alpha}|^2 \tilde{G}_{f\alpha}(k, ik_n) \]  

(2.32)

\[ \tilde{G}_{f\alpha}(k, ik_n) = \frac{1}{ik_n - E_f - \tilde{\Sigma}_{f\alpha}(ik_n)} \]  

(2.33)

Approximate solutions of the energy bands from the linker states are

\[ E_\alpha(k) \approx \varepsilon_\alpha + |V_{k\alpha}|^2 \tilde{G}_{f\alpha}(k, \varepsilon_\alpha) \]  

(2.34)

All of these solutions have the feature that they have replaced the correlated site with a hopping term of the form \( O(V^2G) \). They all have band dispersion: they all have the factor of \( \cos(k) \). This dispersion does not contribute to damping. The Green’s function in eqn.(2.24) is a series of poles. It and the spectral function [10] have the form

\[ G_f(k, E) = \sum_{j=1}^{N+1} \frac{r_j}{E - E_j(k) + i\eta} \]  

(2.35)
\[ A_f(k, E) = -2 \Im \{ G_f(k, E) \} = 2\pi \sum_{j=1}^{N+1} r_j \delta[E - E_j(k)] \]  
\[ r_j = \frac{\Pi_{n=1}^N (E_j - \varepsilon_n) }{\Pi_{\ell=1,\ell\neq j}^{N+1} (E_j - E_\ell)} \]  

where \( r_j \) is the residue of the pole. The collective states \( E_\alpha(k), E_f(k) \) depend upon wave vector, but the wave vector does not give scattering. The local operators do have damping

\[ \langle n_{\ell,s} \rangle = \frac{1}{n} \sum_k \langle n_{k,s} \rangle = \frac{1}{n} \sum_k \int \frac{dE}{2\pi} A_f(k, E)n_F(E) \]  
\[ = \int_{-\pi}^{\pi} \frac{dk}{2\pi} \sum_j r_j n_F[E_j(k)] \]

where \( n_f(E) \) is the Fermion occupation factor.

Next we consider the changes in this expression due to the Hubbard term \( V_h \). We define \( \langle n_{\ell,s} \rangle \) as being evaluated using the exact eigenstates of \( H_0 \). In that case, the first order-perturbation \( \langle V_h \rangle = 0 \). The first contribution is due to second-order perturbation theory. It is introduced into the theory as an additional self-energy in \( \tilde{G} \)

\[ \tilde{G}_{f\alpha}(k, ik_n) = \frac{1}{ik_n - E_f - \tilde{\Sigma}_{f\alpha}(k, ik_n) - \Sigma_U(k, ik_n)} \]  
\[ \Sigma_U(k, ik_n) = \frac{U^2}{n^2} \sum_{pq} S(ik_n; k, p, q) \]  
\[ S(ik_n; k, p, q) = \frac{1}{\beta^2} \sum_{ip, iq} G_f(k + q, ik + iq) G_f(p, ip) G_f(p + q, ip + iq) \]
We use the form in eqn. (2.35) as a summation over poles

\[ S(ik_n; k, p, q) = \sum_{j \in n} r_j r_\ell r_n \frac{n_n(n_j - n_\ell) + n_\ell(1 - n_j)}{ik_n - E_n(k + q) - E_j(p) + E_\ell(p + q)} \tag{2.43} \]

\[ n_j = n_F[E_j(p)], \quad n_\ell = n_F[E_\ell(p + q)], \quad n_n = n_F[E_n(k + q)] \tag{2.44} \]

In evaluating this expression, we assume the energy level scheme shown in fig. 1.4. The \( f \)-level is lower in energy than the states from the linker molecules. Then \( r_f \sim 1 \) while \( r_j \sim V^2/(E_f - E_0)^2 \) for the other bands. We then consider possible values for \( r_j r_\ell r_n \):

- If all three \( (j, \ell, n) \) are in the \( f \)-state the factor \( r_f^3 \) has its largest value. However, all occupation numbers \( n_f \sim 1 \) so the numerator is zero.

- The next largest value of \( r_j r_\ell r_n \) occurs when any two of them are in the \( f \)-level. The only case that has a nonzero numerator is when \( j = n = f \) and \( \ell \neq f \). This gives a contribution

\[ S(ik_n; k, p, q) = r_f^2 \sum_{\ell \neq f} r_\ell \frac{1 - n_\ell}{ik_n - E_f(k + q) - E_j(p) + E_\ell(p + q)} \tag{2.45} \]

Since we are concerned with the self-energy of conduction electrons, the energy denominator (with \( ik_n \to \varepsilon_\alpha \)) is \( O(E_0 - E_f) \). The whole term is of order

\[ \Sigma_U \sim O\left( \frac{U^2V^2}{(E_0 - E_f)^3} \right) \tag{2.46} \]

which we assume is small. It also does not seem very dependent on the wave vector of the conduction band. The main wave vector dependence is through
the numerator $|V_{\kappa\alpha}|^2$.

- The largest terms are when $j = \ell$, so the polarization occurs within the same band. If this band is completely full of electrons, so $n_j = n_\ell$ equals one, then the above expression is zero. It is also zero if the band is empty. Since our interest is in conducting systems, we assume there is one band that is partially filled. Call this band $j = \ell = c$, for conduction band.

\[
\Pi_n^{(1)}(ik_n) = \int \frac{dp}{2\pi i} \frac{n_F[E_c(p)] - n_F[E_c(p + q)]}{ik_n - E_n(k + q) - E_c(p) + E_c(p + q)}
\]

\[
\Pi_n^{(2)}(ik_n) = \int \frac{dp}{2\pi i} \frac{n_F[E_c(p + q)](1 - n_F[E_c(p)])}{ik_n - E_n(k + q) - E_c(p) + E_c(p + q)}
\]

\[
\Sigma_U(k, ik_n) = U^2 r_c^2 \int \frac{dq}{2\pi} \sum_n r_n \{n_F[E_n(k + q)]\Pi^{(1)} + \Pi^{(2)}\}
\]

In order for perturbation theory to be converging, this self energy should be relatively small. Its size depends upon the residues $r_c^2$. They will depend upon the particular band structure. For example, where is the energy level of the correlated site? This self-energy also depends upon wave vector $k$, and contributes to the energy band dispersion.

### 2.4 Higher Dimensions

Our model is easily extended to higher dimensions. First consider two dimensions. We take the crystal structure of the conducting planes of the cuprate superconductors. The correlated sites are in a square lattice, and there is one bridging atom
between them \((N = 1)\). This structure is shown in fig.1.5. The Hamiltonian is

\[
H = E_0 \sum_{i,j,s} \left[ C_{i,j,1,s}^\dagger C_{i,j,1,s} + C_{i,j,2,s}^\dagger C_{i,j,2,s} \right] \\
+ \varepsilon_f \sum_{i,j,s} n_{i,j,s} + U \sum_{i,j} n_{i,j,\uparrow} n_{i,j,\downarrow} \\
+ V \sum_{i,j,s} \left[ f_{i,j,s}^\dagger (C_{i,j,1,s} + C_{i,j,2,s} + C_{i,j-1,1,s} + C_{i-1,j,2,s}) + \text{h.c.} \right]
\]

(2.50)

where the sites are labeled in fig. 2. The site \((i,j)\) is a correlates site, \((i,j,1)\) is the linker in the +\(y\) direction, and \((i,j,2)\) is the linker site in the +\(x\) direction.

We follow the same general steps, for one dimension, and write the Hamiltonian as \(H_0 + V_h\), where \(V_h\) is the Hubbard term. Then a two dimensional lattice transform gives

\[
H_0 = \sum_{k,s} \left\{ E_f f_{k,s}^\dagger f_{k,s} + E_0 \left( C_{k,1,s}^\dagger C_{k,1,s} + C_{k,2,s}^\dagger C_{k,2,s} \right) \\
+ 2V f_{k,s}^\dagger \left[ C_{k,1,s} \cos(k_y/2) + C_{k,2,s} \cos(k_x/2) \right] + \text{h.c.} \right\}
\]

(2.51)

(2.52)

The Green’s function for the correlated site is

\[
G_f(k, ik_n) = \frac{1}{ik_n - E_f - \Sigma_f(k, ik_n)}
\]

(2.53)

\[
\Sigma_f(k, ik_n) = \frac{2V^2}{ik_n - E_0} [2 + \cos(k_x) + \cos(k_y)]
\]

(2.54)

In this case the collective states, and residues, are

\[
E_\pm(k) = \frac{1}{2} \left[ E_0 + E_f \pm \sqrt{(E_0 - E_f)^2 + 8V^2 [2 + \cos(k_x) + \cos(k_y)]} \right]
\]

(2.55)
The two dimensional band structure is evident. The Hamiltonian $H_0$ also has a dispersionless eigenvalue $E_3 = E_0$.

The extension to three dimensions yields a dispersion of

$$2\left[\cos^2(k_x/2) + \cos^2(k_y/2) + \cos^2(k_z/2)\right] = 3 + \cos(k_x) + \cos(k_y) + \cos(k_z)$$

Similar tight-binding dispersion relations can be found for other crystal lattices.

### 2.5 Discussion

We have derived the energy band structure of a periodic system of quantum dots, or molecules, linked by conducting chains of atoms. The quantum dots are regarded as highly correlated. We took the Hubbard model to describe the correlated sites. We assumed that it had a ground state of a spin singlet, in order that all correlated sites have the same ground state. The basic theoretical step is to replace the correlated sites by a transfer term

$$T \approx V^2 G_f$$

where $V$ is the hybridization matrix element, and $G_f$ is the Green’s function for the electrons on the correlated site. We then constructed an accurate approximation to this Green’s function.

The interesting feature of this method is that the bands have only a small amount
of dispersion, and very little damping. This feature is different than found in solutions of the periodic Anderson model. However, our model is different, so should have different solutions. Without the correlated sites, the molecular chains linking them are of finite size, so the system is not conducting. They can only conduct by having electrons hop on, and hop off, of the correlated sites.

We neglect the correlation between correlated sites. The ground state of each correlated site is non magnetic. We also showed that our method is easily extended to two and three dimensions.

There are an unlimited number of possible systems of quantum dots linked by various molecules. Here we have taken a typical system and shown some of its properties. Other arrangements of quantum dots, and linkers, may have quite different energy level arrangements. Those cases will be treated as they are created by experimentalists. If the quantum dot has an odd number of electrons in its ground state, then the dot will have a magnetic moment. There will be a Kondo resonance at low temperatures. This is an interesting case, which is treated in next chapter.
The dynamic mean field theory

3.1 Introduction

Heavy-fermion systems have been shown to have promise for thermoelectric applications both experimentally[3] and theoretically[3, 58]. The advantage of such materials lies in the high thermoelectric coefficient due to the Kondo effect. A similar Kondo effect is present and widely studied in the quantum dots[28, 37, 38, 30, 35, 59]. Nano-engineering can build new materials with arrays of quantum dots[52, 53, 54] that may take advantage of their Kondo effect for high thermoelectric coefficient. Other properties of the materials, including conductivity and thermal conductivity can be tailored to improve the overall performance. An example of such nano-engineered materials, crystalline arrays of quantum dots connected by conducting chains of linkers, is proposed. A prototype of such material is under study in Badding’s group[55]. The possible advantages of this material include better electrical conductivity due to the linker atoms, lower thermal conductivity due to the heavy mass of quantum dots, and higher thermoelectric coefficient due
to the Kondo effect. These possible properties make the material interesting for thermoelectric applications.

In our theoretical model, we treat every quantum dot as an Anderson impurity in the periodic Anderson model (PAM)\cite{28, 37, 38}. Electrons in these sites are strongly correlated due to the on-site Coulomb interaction. These sites are called correlated sites. In the linker sites between quantum dots, such Coulomb interaction is absent. So they are treated as sites in a simple tight binding model. This theoretical model can be considered as an extension of the Hubbard model by adding to it non-interacting linker sites. The difference of this model to Hubbard model and periodic Anderson model has been explained in the first chapter.

The model is studied in the infinite dimensional cubic lattice with dynamical mean field theory (DMFT) in this chapter. The DMFT becomes exact for such infinite dimensional lattice model\cite{51} and is widely used for lattice models with strong interactions\cite{51, 60}. For our study, the infinite dimensional cubic lattice is divided into two sublattices, which can be constructed according to following rule: the nearest neighbors of any given site are assigned to the opposite lattice. The two dimensional example is shown in Fig.3.1. One sublattice is occupied by conducting linkers. And the other sublattice is occupied by the correlated sites. The effective single-impurity Anderson model (SIAM) from the mapping of this lattice model is solved by Wilson’s numerical renormalization group (NRG)\cite{26}. The advantage of this impurity solver lies in its accuracy for the low-energy properties\cite{62}, which is essential for this study. The self-consistency calculation is done at zero temperature. Transport properties at finite temperature are interesting. At temperatures much lower than the Kondo temperature $T_K$, the spectral functions and self energies can be approximated by the corresponding zero temperature results. With such approximations, we can discuss the transport properties for our model using
Figure 3.1. The two dimensional version of the lattice considered in this study. The lattice we studied in this chapter is the infinite dimensional extension of it.

Kubo formulas at low temperature. The details of the theory are given in the next section.

We work in the paramagnetic phase. The local spectral function, optical conductivity and Seebeck coefficient are studied. This study highlights the possibility of quantum dot arrays for thermoelectric applications.

3.2 Theory

The Hamiltonian for our model is given by

$$H = \sum_{i\sigma} [ (\epsilon_f - \mu) f_{i\sigma}^\dagger f_{i\sigma} + \frac{U}{2} f_{i\sigma}^\dagger f_{i\sigma} f_{i-\sigma}^\dagger f_{i-\sigma} ]$$

$$+ \sum_{i\sigma} (\epsilon_f - \mu) C_{i\sigma}^\dagger C_{i\sigma} + \sum_{i\sigma} t^* C_{i+\delta\sigma}^\dagger f_{i\sigma} + h.c) \quad (3.1)$$
Where \( f_{i\sigma}(f_{i\sigma}^\dagger) \) destroys (creates) an electron with spin \( \sigma \) and binding energy \( \epsilon_f \) at correlated site \( i \). \( \mu \) is the chemical potential. \( U \) denotes the on-site Coulomb interaction. Similarly, \( C_{i\sigma}(C_{i\sigma}^\dagger) \) destroys (creates) an electron with spin \( \sigma \) and binding energy \( \epsilon_c \) at linker site \( i \). The last term describes the coupling between correlated sites and linker sites with matrix element \( t^* \). For correlated site \( i \), \( i + \delta \) denotes the nearest linker sites. The two dimensional version of this lattice is shown in Fig.3.1. In order to have a nontrivial density of states, \( t^* \) must scale with \( 1/\sqrt{d}[51] \), where \( d \) is the dimension of the lattice. We put \( t^* = t/\sqrt{2d} \) in this study.

We assume the presence of some external bath that keeps the chemical potential constant. This constant can be absorbed in \( \epsilon_f \) and \( \epsilon_c \), and \( \mu \) is dropped in the following formulas.

We take the distance between the nearest neighbor sites to be the unit for distance. The nearest sites for site \( i(x_1,x_2,x_3,\cdots) \) can be put as:

\[
\begin{align*}
    i + \delta_{\pm 1} &= (x_1,x_2,x_3,\cdots) + (\pm1,0,0,\cdots); \\
    i + \delta_{\pm 2} &= (x_1,x_2,x_3,\cdots) + (0,\pm1,0,\cdots); \\
    i + \delta_{\pm j} &= (x_1,x_2,x_3,\cdots) + (0,0,\cdots,\pm1(jth),\cdots);\cdots;
\end{align*}
\]

The vectors between neighbors define all possible lattice vectors.

\[
\begin{align*}
    a_1 &= \delta_{-2} - \delta_{-1} = (1,-1,0,\cdots) \\
    a_2 &= \delta_{+2} - \delta_{-1} = (1,1,0,\cdots) \\
    a_j &= \delta_{+j} - \delta_{-1} = (1,0,\cdots,1(jth),\cdots)
\end{align*}
\]
The unit vectors $b_i$ in momentum space (reciprocal lattice) are determined by

$$b_i \cdot a_j = 2\pi \delta_{i,j} \quad (3.2)$$

With the above formulas, the non interacting Hamiltonian in momentum space is

$$H_0 = \sum_{k,\sigma} \left[ \epsilon_f f_{k\sigma}^\dagger f_{k\sigma} + \epsilon_c C_{k\sigma}^\dagger C_{k\sigma} + (V_k C_{k\sigma}^\dagger f_{k\sigma} + h.c) \right] \quad (3.3)$$

$$k = \sum_i \frac{k_i b_i}{2\pi}; k_i = \frac{1}{N}, \frac{2}{N}, \frac{3}{N}, \ldots \quad (3.4)$$

$$V_k = t^* (1 + e^{i(k_1+k_2)} + \sum_{j=1}^{\infty} e^{ik_j} + \sum_{j=3}^{\infty} e^{i(k_1+k_2-k_j)}) \quad (3.5)$$

$$= t^* \left\{ e^{ik_1} + e^{ik_2} + e^{i(k_1+k_2)/2} \left[ (e^{i(k_1+k_2)/2} + \sum_{j=3}^{\infty} e^{i(k_1+k_2-2k_j)/2}) + h.c \right] \right\}$$

Here $N$ is the number of unit cells in one axis. Considering $k_i$ as random numbers between 0 and 1, the $|V_k|$ obeys Gaussian distribution function:

$$P(|V_k|) = \frac{1}{\sqrt{2\pi t^2}} e^{-\frac{|V_k|^2}{2t^2}} \quad (3.6)$$

The exact lattice Green’s functions can be expressed as:

$$G_{kf}(\omega) = \frac{1}{\omega - \epsilon_f - \Sigma_f(k) - \frac{|V_k|^2}{\omega - \epsilon_c}} \quad (3.7)$$

$$G_{kc}(\omega) = \frac{1}{\omega - \epsilon_c - \Sigma_f(k) - \frac{|V_k|^2}{\omega - \epsilon_f - \Sigma_f(k)}} \quad (3.8)$$

Where $\Sigma_f(k)$ is the $f$ electron self energy resulting from the Coulomb interaction. Within DMFT, $\Sigma_f(k)$ is approximated by the interaction induced self energy $\Sigma_f$. 
of the effective SIAM. The Green’s function for the corresponding effective SIAM is given by:

\[ G_{ef}(\omega) = \frac{1}{\omega - \epsilon_f - \Sigma_f - \Delta(\omega)} \] (3.9)

Where \( \Delta(\omega) \) is the hybridization function, which is determined by the self-consistency condition of DMFT. The self-consistency condition states the on-site (local) Green’s function for the model should be equal to the Green’s function of the effective SIAM:

\[ G_{ef}(\omega) = \frac{1}{N} \sum_k G_{fk}(\omega) = \int \frac{P(|V_k|)d|V_k|}{\omega - \epsilon_f - \Sigma_f + i\delta - |V_k|^2} \] (3.10)

For numerical reasons\[58, 66\], an extra small imaginary self energy \( \delta \) has been added to the \( f \) electron Green’s function in the above formula for particle-hole asymmetrical cases. This extra self energy \( \delta \) can be considered as the self energy due to impurity scattering. This term turns out to affect the transport properties, as suggested by its physical explanation.

The self consistent calculations are conducted as follows. For a given self energy \( \Sigma_f \), the hybridization function \( \Delta(\omega) \) is determined by the self consistency equation (3.10). Then NRG\[26, 63, 64, 65\] is applied to calculate the spectral functions. The real part of the Green’s functions are obtained from standard Kramers-Kronig transformation. The self energy \( \Sigma_f \) is determined by the ratio of two Green’s functions as\[66\]:

\[ \Sigma_f = U \frac{F(\omega)}{G_{ef}(\omega)} \] (3.11)
Where \( F(\omega) = \ll f_\sigma f_{-\sigma} f_\sigma^\dagger f_{-\sigma}^\dagger \gg (\omega) \). The self consistency condition and self energy are used to update the hybridization function \( \Delta(\omega) \). The above steps are repeated until the self consistency is achieved.

The current operator is\[10\]:

\[
\vec{j} = -it^* \sum_{i,\delta} (\delta f_{i+\delta}^\dagger C_i + \delta C_{i+\delta}^\dagger f_i)
\tag{3.12}
\]

Where \( \delta \)s are the same as those in the Hamiltonian. The operator can be written in momentum space as:

\[
\vec{j} = \sum_{x_i} \left[-2t \sum_k \sin(k \cdot x_i) e^{i(k \cdot x_0 + \phi)} f_k^\dagger C_k + h.c\right] \hat{x}_i
\tag{3.13}
\]

Where \( x_i = (0, 0, \cdots, 1(ith), \cdots) \). \( \hat{x}_i \) is the unit vector in \( x_i \) direction. \( x_0 \) and \( \phi \) are two constants.

The optical conductivity can be expressed as the current-current correlation as\[67\]:

\[
d\sigma(\omega) = \frac{1}{i\omega N} \sum_{\hat{x}_i} \ll j_{\hat{x}_i} j_{\hat{x}_i} \gg
\tag{3.14}
\]

In the \( d \to \infty \) limit, the current operator vertex corrections vanish. The correlation function can be evaluated straightforwardly\[67\]. The following formula is derived for the optical conductivity:

\[
\sigma(\omega) = \frac{2\pi t^2}{d} \int dk \int d\epsilon P(|V_k|) A_f(|V_k|, \epsilon) \frac{1}{2} \left[ A_c(|V_k|, \epsilon + \omega) n_F(\epsilon) - n_F(\epsilon + \omega) \omega + A_c(k, \epsilon - \omega) n_F(\epsilon) - n_F(\epsilon - \omega) \frac{\omega}{-\omega} \right]
\tag{3.15}
\]
Where $A_f(|V_k|,\omega) = -ImG_{kf}(\omega)/\pi$, $A_c(|V_k|,\omega) = -ImG_{kc}(\omega)/\pi$ are spectral functions. $n_F$ is the Fermi distribution function. $P(|V_k|)$ is defined in equation (3.6). The transport distribution function as defined in the ref. ([57]) (also known as generalized relaxation time) can be identified with the above equation to be:

$$
\tau(\omega) = \frac{2\pi}{d t^2} \int_{-\infty}^{\infty} P(|V_k|) A_f(|V_k|,\omega) A_c(|V_k|,\omega) dk
$$

(3.16)

The Seebeck coefficient can be expressed as the ratio between two linear transport coefficients as [58]:

$$
L_{11} = \frac{e^2}{\hbar} \int_{-\infty}^{\infty} \left[-\frac{dn_F(\omega)}{d\omega}\right] \tau(\omega) d\omega
$$

(3.17)

$$
L_{12} = \frac{e}{\hbar} \int_{-\infty}^{\infty} \left[-\frac{dn_F(\omega)}{d\omega}\right] \omega \tau(\omega) d\omega
$$

(3.18)

$$
S = \frac{k_B e L_{12}}{k_B T L_{11}} \frac{1}{L_{11}} = 86 \frac{e L_{12}}{k_B T L_{11}} \frac{1}{(\mu V/K)}
$$

(3.19)

The absolute value of Seebeck coefficient can be derived from the above formulas as long as $\tau(\omega)$ is known.

As indicated by the above formulas, transport properties can be discussed only at nonzero temperature. At temperatures much lower than the Kondo temperature $T_K$, it is reasonable to believe the spectral functions and self energies can be approximated by the corresponding zero temperature results. The model we consider has a very high Kondo temperature, which can be estimated by [63]:

$$
k_B T_K = (\Delta(0)U/2)^{1/2} e^{\pi \epsilon_f (\epsilon_f + U)/2 \Delta(0) U}
$$

(3.20)
As all terms, including \( \Delta(0) \), are of the same order, \( k_B T_K \) is roughly of the order \( 0.1 U \). We can calculate the transport coefficients with Kubo formulas for temperature much lower than \( 0.1 U \). Typically, a temperature smaller than \( 0.01 U \) is used for following calculations.

### 3.3 Results

The calculation was done for different sets of parameters \((\epsilon_f, \epsilon_c, U)\). The parameters are chosen to satisfy \((\epsilon_f + \text{Re}\Sigma_f(0))\epsilon_c > 0\). Such a parameter set avoids a gap across the chemical potential in the hybridization function \( \Delta(\omega) \). The cases with a gap across the chemical potential in the hybridization function require extra complicated treatments, which is left out of this paper. The results shown below are typical for our calculations.
Figure 3.3. The on-site spectral function for the particle-hole asymmetrical case. The inset is the imaginary part of hybridization function $\Delta(\omega)$. The parameters are $t = 1; U = 3; \epsilon_f = -2.5; \epsilon_c = -0.5$. Unit for $\omega$ is $5t$.

### 3.3.1 Spectral function

A typical $f$ electron local spectral function for the particle-hole symmetrical case is shown in Fig.3.2. $t = 1, U = 4$ have been chosen for the plot. The local spectral function for Hubbard model with the same parameters is shown for comparison. For the Hubbard model, the one-particle spectrum develops the typical three-peak structure with a quasiparticle peak at $\omega = 0$ and the two Hubbard bands at $\pm U/2$. Three-peak structure is also obtained for our model. But the quasiparticle peak is broadened. The two Hubbard bands shrunk and shifted outward. The Hubbard bands start at $\pm U/2$, instead of having a maximum there. This increases the weight of the quasiparticle in our model, which is important for getting better conductivity.

A typical self-consistent $f$ electron local spectral function for the particle-hole asymmetrical case is shown in Fig.3.3. $t = 1; U = 3; \epsilon_f = -2.5; \epsilon_c = -0.5$ has been chosen for the parameters. The spectral function has a five-peak structure. Three peaks are similar to the peaks of the single impurity Anderson model or
Figure 3.4. The optical conductivity for the particle-hole symmetrical case. The black dots is for our model. The blue (gray) dots are for the Hubbard model. The parameters are $t = 1; U = 4$. Unit for $\omega$ is $10t$.

Hubbard model. The negative peak around chemical potential is the quasiparticle peak due to the Kondo effect. Similar to the symmetrical case the Hubbard bands start at band energy $\epsilon_f, \epsilon_f + U$, instead of having a maximum there. There are two extra peaks corresponding to the peaks in the hybridization function. The hybridization function is shown in the inset of Fig.3.3. The two extra peaks are produced by the peaks of the electron bands. For single impurity Anderson model, the coupling between the impurity and the band is weak. The structure of the band does not show up in the f electrons spectral function. In our model, the coupling is comparable to the band width and Coulomb interaction. There are two extra peaks due to the structure of the bands.

### 3.3.2 Optical conductivity

The optical conductivity for the symmetrical case is shown in Fig.3.4. In the same plot, the optical conductivity for the Hubbard model is shown. The peak at nonzero frequency corresponds to the transition between quasiparticle peak and the Hubbard bands. The positions agree with the peaks in spectral functions. The
peaks around the zero frequency are Drude peaks, corresponding to the transitions inside the quasiparticle peaks. The presence of Drude peaks suggest the solutions for the models are metallic. As indicated by the higher Drude peak, the conductivity of our model should be better than that of the Hubbard model. This suggests that the inclusion of the linker sites does increase the conductivity of the material. The optical conductivity for an asymmetrical case is shown in Fig. 3.5. The basic feature is the same as the symmetrical case.

The Hubbard model is well known to show a metal-insulator transition with increasing interaction $U$[51, 66, 68]. We do not find such transition in our model with particle-hole symmetry. The Drude peaks are always present in the calculation of our model. Based on our calculation and the following theoretical arguments, we believe there is no metal-insulator transition for our model in the symmetrical case.

For the symmetrical case, we have:

$$
\epsilon_c = 0
$$

(3.21)

$$
-\epsilon_f - \Sigma_f = c_1 \omega + ic_2 \omega^2
$$

(3.22)
Where \( c_1, c_2 \) are two constants. The second equation results from the exact relation for \( f \) electron’s self energy around the chemical potential[69]. The linker’s lattice Green’s function is reduced to:

\[
G_{kc} = \frac{1}{\omega - \frac{|V_k|^2}{\omega(1+c_1)+ic_2\omega^2}}
\]  

(3.23)

For \( |\omega| \ll (1 + c_1)/c_2 \), the imaginary part of the self energy can be neglected. It is obvious that the poles near the chemical potential for the linker’s lattice Green’s function just get normalized by the interaction. These poles form an energy band around chemical potential. Due to the particle-hole symmetry, this band is half filled. According to band theory, this half filled band is a conducting band. So the model we are considering must always be metallic. If the metal-insulator transition took place, in the insulator phase the \( f \) electron’s self energy can be approximated by \(-\epsilon_f - \Sigma_f \approx c_1/\omega + i(c_2\omega^2 + \delta(\omega))\) according to Bulla’s work[66]. Substituting the above self energy in equation (23), we will still get a conducting band with similar arguments. This result contradicts the assumption that the solution is in the insulator phase. This contradiction means that metal-insulator should not take place at all. The above arguments justify the following physical picture: the electron’s spectral function in the linker sites is just broaden by coupling to other sites. These linker sites still behave as periodic potential wells for electrons as in the tight binding model. An extended conduction band should be expected for the model.
3.3.3 Seebeck coefficient

The Seebeck coefficient is determined by the transport distribution function $\tau(\omega)$ [57]. The Seebeck coefficient is related to the asymmetry of the electron bands[3]. For the symmetrical case, there is no asymmetry in the band. The Seebeck coefficient is zero. For the asymmetrical case, a typical transport distribution function of our model is shown in Fig.3.6. As shown in the plot, $\tau(\omega)$ is strongly affected by the extra self energy $\delta$ in equation (11). But different reasonable small $\delta$s produced almost the same $f$ electron spectral functions. This agrees with the physical interpretation of $\delta$ as coming from impurity scattering, which just affect the transport properties but not the electron bands. The $\tau(\omega)$ of our model always show a single asymmetrical peak near the chemical potential. As proved before by Mahan and Sofo[57], $\tau(\omega)$ in the shape of Dirac delta function located at $2.4k_B T$ above or below the chemical potential can achieve the best efficiency for the thermoelectric application. Based on that theory and the shape of $\tau(\omega)$ in our model, it is reasonable to believe that high efficiency for thermoelectric applications can be achieved in quantum dot arrays. And the best operational temperature is around $\omega_p/2.4k_B$, where $\omega_p$ is the position of the peak in $\tau(\omega)$

The Seebeck coefficient is the ratio between two coefficients with proper units. The absolute value of Seebeck coefficient can be determined. For the example shown in Fig.3.6, $\omega_p \approx 0.005$. This model will give the highest figure of merit around the temperature $k_B T = \omega_p/2.4 \approx 0.002$ according to above arguments, which is much lower than the Kondo temperature $k_B T_K \approx 0.06$. The Seebeck coefficients calculated at the above temperature are 42, 50, 64, 106$\mu V/K$ respectively for $\delta = 0.0057U, 0.0056U, 0.0055U, 0.0054U$. Obviously, smaller $\delta$ is better for thermoelectric applications. $\delta$ shouldn’t depend much on the dimension of the
Figure 3.6. The transport distribution function for the particle-hole asymmetrical case. The $\delta = 0.0057U, 0.0056U, 0.0055U$ for red, blue and green plot respectively. The other parameters are $t = 1; U = 3; \epsilon_f = -2.5; \epsilon_c = -0.5$. Unit for $\omega$ is $5t$.

The model under consideration, as it comes from impurity scattering, which is a local incoherent process. A high Seebeck coefficients with small $\delta$ can be achieved in real materials, such as high quality crystals made of quantum dot arrays with few impurities[55]. The low temperature maximum Seebeck coefficient for the corresponding Hubbard model (with the same $t, \epsilon_f$ and $U$) is $51\mu V/K$, which agrees with previous a study of the Hubbard model[70]. Compared with the Hubbard model, the Seebeck coefficients of our model increases when $\delta$ is small.

For a different set of parameters, the Seebeck coefficient tends to increase when $\epsilon_f + Re\Sigma_f(0)$ is closer to the chemical potential. We found the Seebeck coefficient to be as high as $200\mu V/K$ for the parameter set of $t = 1, U = 2, \epsilon_f = -1.5, \epsilon_c = -0.5$. As the self energy $\delta$ is used in these calculations, the dependence of the Seebeck coefficient on the parameters are not very conclusive. Further study is necessary to identify the parameter dependence of transport coefficients. But it is safe to draw the conclusion that the Seebeck coefficients are always quite high for the cases with small $\epsilon_c$ and $|\epsilon_c| > |\epsilon_f + Re\Sigma_f(0)|$. These data highlight the potential of quantum dot arrays for thermoelectric applications.
3.4 Conclusion

Based on above study, it is obvious that the model we studied is quite different from the Hubbard model. This difference is non-trivial. The metal-insulator transition in other strongly correlated models is absent in our model. Probably the phase diagram of our model will also be quite different from the Hubbard model due to different correlation in nearby correlated sites. Our model shows a high Seebeck coefficient and good conductivity, which indicates the possible good thermoelectric properties for arrays of quantum dots.

3.5 Acknowledgments

"Numerical renormalization group calculations were performed using the "Ljubljana NRG" code."
Temperature variations of the resistivity and Seebeck coefficient in the periodic Anderson model

4.1 Introduction

There has been substantial interest in the rare-earth compounds for the past decades [9, 71]. One reason for this is their large Seebeck coefficient, which makes them candidates for good thermoelectric materials[3]. Understanding the properties of these rare-earth compounds is an interesting and challenging task. Theoretically, the rare-earth compounds can be described by the Periodic Anderson model (PAM). The PAM has been studied extensively[72, 73, 74, 75, 76, 51, 58]. The results from these studies show good agreements with the experiments. But most of these solutions depend heavily on numerical calculations. An analytic ex-
act solution is still not available. Based on dynamic mean field theory [51, 58], we develop some analytical results for the temperature variations of the resistivity and Seebeck coefficient. Our results agree with the formulas in the two band model [79], which is an empirical model showing good agreement with the transport measurements of rare-earth compounds [79, 85, 86, 87]. We compare our results with data reported in the literature. Good agreements are found in the low temperature region. These formulas are comprehensive results and shed additional light on the transport properties of the rare-earth compounds. Especially they show how large Seebeck coefficient can be obtained. The importance of a moderate imaginary part of the $f$ electron’s self energy ($Im\Sigma_f$) caused by the interaction is highlighted for obtaining a large Seebeck coefficient. The temperature $T_o$ at which the resistivity is a maximum is considered to be the onset temperature for the coherent of $f$ electrons [77]. Based on our theory, we also propose that $0.1T_o$ is a good estimate for the Kondo temperature.

4.2 Theory

Our analytical theory is based on numerical results from the dynamical mean field theory (DMFT). We consider the infinite dimension cubic lattice in this study. The Hamiltonian of the periodic Anderson model is given by:

$$H = \sum_{k,\sigma} [\epsilon_{f} f_{k\sigma}^\dagger f_{k\sigma} + \epsilon_{k} C_{k\sigma}^\dagger C_{k\sigma} + (VC_{k\sigma}^\dagger f_{k\sigma} + h.c)] + U \sum_{i} n_{i\sigma}^f n_{i\sigma}^{f \dagger}$$ (4.1)

$$n_{i\sigma}^f = f_{i\sigma}^\dagger f_{i\sigma}$$ (4.2)
Where \( f_{k\sigma}(f_{k\sigma}^\dagger) \) destroys (creates) a correlated \( f \) electron with wave vector \( k \), spin \( \sigma \) and energy \( \epsilon_f \). \( U \) denotes the Coulomb interaction between two \( f \) electrons at the same site. Similarly, \( C_{k\sigma}(C_{k\sigma}^\dagger) \) destroys (creates) a conduction \( s-d \) electron with wave vector \( k \), spin \( \sigma \) and energy \( \epsilon_k \). The \( f \) electrons hybridize with the conduction electrons via the matrix element \( V \). We assume a Gaussian density of states for the unperturbed conduction-electron system:

\[
\rho(\epsilon_k) = \frac{e^{-(\epsilon_k/t)^2/2}}{t\sqrt{2\pi}}
\]

Here \( t \) is a constant. \( \sqrt{2}t \) is the effective band width of the conduction electrons. The exact conduction electron’s Green’s function can be obtained for the PAM as:

\[
G_{kc}(\omega) = \frac{1}{\omega - \epsilon_k - \Sigma_c(\omega)}
\]

\[
\Sigma_c(\omega) = \frac{|V|^2}{\omega - \epsilon_f - \Sigma_{fk}(\omega)}
\]

Where \( \Sigma_{fk}(\omega) \) is the \( f \) electron’s self energy resulting from the Coulomb interaction \( U \). Within DMFT, \( \Sigma_{fk}(\omega) \) is approximated by the interaction induced self energy \( \Sigma_f(\omega) \) of the effective single impurity Anderson model (SIAM). The Green’s function for the corresponding effective SIAM is given by:

\[
G_{ef}(\omega) = \frac{1}{\omega - \epsilon_f - \Sigma_f(\omega) - \Delta(\omega)}
\]

Where \( \Delta(\omega) \) is the hybridization function, which is determined by the self-consistency condition of DMFT. We note that all correlations caused by the Coulomb interaction are described by this self energy \( \Sigma_f(\omega) \). There is now no analytical
Figure 4.1. The imaginary part of f electron’s self energy calculated by DMFT [58]. It is shown here that this part is proportional to \( \sqrt{T} \).

result for this self energy \( \Sigma_f(\omega) \). But it is well known that there is only one energy scale in the SIAM, which is the Kondo temperature. Many quantities in the SIAM show universal behaviors[26, 78]. We expect such an universal behavior for the \( f \) electron’s self energy. The quasi-elastic neutron-scattering line-width of SIAM has a universal behavior. The line-width is roughly proportional to \( T^{1/2} \) at low temperature[78, 22, 79]. The line-width can be considered to be an approximation of the \( f \) electron’s life time. So we propose the following form for the imaginary part of the self energy:

\[
Im \Sigma_f(\omega) = c_1(\omega) + c_2(\omega)T^{1/2}
\]  

(4.7)

Where \( c_1(\omega) \) and \( c_2(\omega) \) are two functions independent of temperature. \( T \) denotes the temperature. The first order derivation of \( Im \Sigma_f \) is zero at chemical potential according to the properties of the Fermi liquid[69]. This form is confirmed by a recent DMFT calculation, as show in Fig.4.1 [58]. The real part of self energy is
given by:

\[ Re \Sigma_f(\omega) = Re \Sigma_f(\mu) + \frac{\partial Re \Sigma_f(\omega)}{\partial \omega} (\omega - \mu) = Re \Sigma_f(\mu) + (1 - z^{-1})(\omega - \mu) \quad (4.8) \]

Here \( z^{-1} = 1 - \frac{\partial Re \Sigma_f(\omega)}{\partial \omega} \) is the mass enhancement factor. \( \mu \) is the chemical potential.

The transport properties of the PAM are calculated within the linear response theory with the Kubo formulas. The conductivity and Seebeck coefficient are given by[58]:

\[
\sigma(T) = \frac{e^2}{\hbar a} \int_{-\infty}^{\infty} [-f'(\omega)] \tau(\omega) d\omega \quad (4.9)
\]

\[
S(T) = \frac{1}{T \sigma \hbar a} \int_{-\infty}^{\infty} [-f'(\omega)](\omega - \mu) \tau(\omega) d\omega \quad (4.10)
\]

Where \( f(\omega) \) is the Fermi distribution function. \( a \) is the lattice constant. \( e \) and \( \hbar \) have their usual meanings. \( \tau(\omega) \) is the generalized relaxation time defined as:

\[
\tau(\omega) = \frac{2\pi t^2}{d} \int_{-\infty}^{\infty} \rho(\epsilon_k)(-\frac{Im G_{kc}}{\pi})^2 d\epsilon_k \\
= \frac{2t^2}{d\pi} \int_{-\infty}^{\infty} \rho(\epsilon_k) \left[ \frac{Im \Sigma_c(\omega)}{(\omega - \epsilon_k - Re \Sigma_c(\omega))^2 + Im \Sigma_c(\omega)^2} \right]^2 d\epsilon_k \quad (4.11)
\]

Here \( d \) is the dimension of the lattice. The self energy usually is much smaller than the band width, which means \( Im \Sigma_c(\omega)/t \ll 1 \). So we have:

\[
\tau(\omega) = \frac{t}{\sqrt{2\pi d Im \Sigma_c(\omega)}} e^{-\frac{[\omega - Re \Sigma_c(\omega)]^2}{2t^2}} \times \left\{ 1 - \left[ \frac{1}{2} + \frac{3}{2} \frac{[\omega - Re \Sigma_c(\omega)]^2}{2t^2} \right] \left[ \frac{Im \Sigma_c}{t} \right]^2 + O \left[ \frac{Im \Sigma_c}{t} \right]^3 \right\} \\
\approx \frac{t}{\sqrt{2\pi d Im \Sigma_c(\omega)}} e^{-\frac{[\omega - Re \Sigma_c(\omega)]^2}{2t^2}} \quad (4.12)
\]
The temperature $T$ is also very small compared to the band width. This is the case at least for the low temperature region we are interested in. We can ignore terms of order $k_B T/t$. $\tau(\omega)$ then is expanded in a Taylor series around the chemical potential $\mu$ as:

$$
\tau(\omega) \approx e^{\frac{[\mu - Re\Sigma_f(\mu)]^2}{2t^2}} \frac{t}{\sqrt{2\pi V^2 d}} \left\{ Im\Sigma_f(\mu) + \frac{\bar{\epsilon}_f^2}{Im\Sigma_f(\mu)} \right. \\
\left. - \frac{2z^{-1}\bar{\epsilon}_f}{Im\Sigma_f(\mu)}(\omega - \mu) + \frac{LT(\mu)}{2Im\Sigma_f(\mu)}(\omega - \mu)^2 \right\} \quad (4.13)
$$

Where $\bar{\epsilon}_f$ is the $f$ electron’s resonance position given by:

$$
\bar{\epsilon}_f = \epsilon_f + Re\Sigma_f(\mu) - \mu \quad (4.14)
$$

And,

$$
LT(\mu) = 2z^{-2} + Im\Sigma_f(\mu)[Im\Sigma_f(\mu)]'' \left( 1 - \frac{\bar{\epsilon}_f^2}{Im\Sigma_f^2(\mu)} \right) \quad (4.15)
$$

We use a Sommerfeld expansion for the integrals.

$$
\int_{-\infty}^{\infty} A(\omega)[-f'(\omega)]d\omega = A(\mu) + \frac{\pi^2}{6}(k_B T)^2 A''(\mu) + O(T^3) \quad (4.16)
$$

Conductivity and Seebeck coefficient are found to be:

$$
\sigma(T) \approx e^{\frac{[\mu - Re\Sigma_f(\mu)]^2}{2t^2}} \frac{e^2 t}{\hbar d \sqrt{2\pi V^2 d}} \left\{ Im\Sigma_f(\mu) + \frac{\bar{\epsilon}_f^2 + LT(\mu)(\pi k_B T)^2}{6 Im\Sigma_f(\mu)} \right\} \quad (4.17)
$$

$$
S(T) \approx \frac{1}{T\sigma(T)\hbar a} \frac{e}{3} \tau'(\mu)
$$
\[
\frac{1}{\sigma(T)} \frac{e^{-2z^{-1}\bar{\varepsilon}_f(\pi k_B)^2}}{\hbar a} \frac{T}{3 \text{Im} \Sigma_f(\mu)} = \frac{-2z^{-1}\bar{\varepsilon}_f(\pi k_B)^2T}{3e} \left\{ \text{Im} \Sigma_f^2(\mu) + \bar{\varepsilon}_f^2 + LT(\mu)(\pi k_B T)^2 \right\}
\] (4.18)

At the low temperature region \( T < 10T_K \), where \( T_K \) is the Kondo temperature for the effective SIAM, \( \bar{\varepsilon}_f \) and \( z^{-1} \) have little temperature variations\[58\], which can be neglected. With equation (4.7), above formulas give the analytic results for the temperature variations of the resistivity and Seebeck coefficient.

### 4.3 Discussions

#### 4.3.1 Comparison with the experiments

At the low temperature region \( T < 10T_K \), \( \bar{\varepsilon}_f \) and \( z^{-1} \) are roughly constants\[58\]. \( T/[S(T)\sigma(T)] \) is proportional to \( \text{Im} \Sigma_f(\mu) \). With the proposed temperature dependence for \( \text{Im} \Sigma_f(\mu) \), \( T/[S(T)\sigma(T)] \) should be proportional to \( \sqrt{T} \). We use the resistivity and Seebeck coefficient data of rare-earth compounds in the literature\[80, 81, 82, 83, 84\] and plot them as \( T/[S(T)\sigma(T)] \) versus \( \sqrt{T} \). Linear regions as shown by our theory are indeed found at the low temperature part of the plot, as shown in Fig.4.2.

With further assumption that \( LT(\mu)(k_B T)^2 \ll \bar{\varepsilon}_f^2 \), equation (4.17) and (4.18) are simplified to:

\[
\sigma(T) = b \left[ \text{Im} \Sigma_f(\mu) + \frac{\bar{\varepsilon}_f^2}{\text{Im} \Sigma_f(\mu)} \right]
\] (4.19)

\[
S(T) = cT/\left[ \text{Im} \Sigma_f(\mu)^2 + \bar{\varepsilon}_f^2 \right]
\] (4.20)
Figure 4.2. The $\frac{T}{S(T)/\pi(T)}$ are plot versus $\sqrt{T}$. The unit for $\frac{T}{S(T)/\pi(T)}$ is arbitrary. The data in the bottom plot comes from DMFT calculation[58]. The experiment data are from refs. [80, 81, 82, 83, 84]

Where $b, c$ are constant coefficients. Above results are the same as the transport formulas for the two band model[79] with the scattering width $W(T)$ given by $\alpha Im \Sigma_f(\mu)$, where $\alpha$ is another constant. The two band model has shown good agreement with the transport measurements[79, 85, 86, 87]. In the two band model, the scattering width is given by $(k_1 + k_2 T^{1/2})e^{-(k_1 + k_2 T^{1/2})/T}$. Such a form for scattering width can not be obtained naturally in our theory. But we do notice that with a proper constant $a$, in the temperature region around the maximum of the resistivity, we have:

$$\frac{|a + k_2 T^{1/2} - (k_1 + k_2 T^{1/2})e^{-(k_1 + k_2 T^{1/2})/T}|}{(k_1 + k_2 T^{1/2})e^{-(k_1 + k_2 T^{1/2})/T}} < 5\%$$

(4.21)
So our results are in good agreement with the empirical two band model. Including the temperature dependence of $z^{-1}$ and $\bar{\epsilon}_f$ can lead to formulas that agree better with the two band model. But this leads to complex formulas with lots of unknown coefficients, which we do not want to discuss. And in general, we do not believe the scattering width $W(T)$ used in the literature for experimental fitting is the exact form. Our theory shows some clues in understanding these phenomenal transport formulas.

### 4.3.2 Seebeck coefficient

It is interesting to show how we can have large Seebeck coefficients from the PAM. First, it is important to have the resonance position $\bar{\epsilon}_f$ with a value not much larger than $k_B T$. In the case $|Im \Sigma_f(\mu)| > |\bar{\epsilon}_f|$, we have $S(T) < O(k_B T / |\bar{\epsilon}_f|) \frac{k_B}{e}$. The Seebeck coefficient is of the order $k_B T / \bar{\epsilon}_f$, which would be small if above requirement was not satisfied. In the other case $|Im \Sigma_f(\mu)| < |\bar{\epsilon}_f|$, based on equation (4.15) and (4.18), We have:

$$|S(T)| \leq \frac{2\pi k_B}{\sqrt{3} e} \left( \frac{z^{-1} \pi k_B T}{\sqrt{3}} \right) |\bar{\epsilon}_f| / \left[ \left( \frac{z^{-1} \pi k_B T}{\sqrt{3}} \right)^2 + \bar{\epsilon}_f^2 \right] \leq \frac{\pi k_B}{\sqrt{3} e}$$  \hspace{1cm} (4.22)

The maximum Seebeck coefficient can be obtained only if $\bar{\epsilon}_f \sim z^{-1} k_B T$. So for both cases, a large Seebeck coefficient can be obtained only with $\bar{\epsilon}_f$ not much larger than $K_B T$.

Second the imaginary part of self energy $Im \Sigma_f(\mu)$ from the Coulomb interaction should not be too small. Due to phonon and impurity scattering, another self
energy \( i \delta_c \) should be included in \( \Sigma_c \). The Seebeck coefficient is modified to be:

\[
S'(T) = \frac{S(T)}{1 + \frac{\delta_c(\text{Im}\Sigma_f^2(\mu) + \bar{\epsilon}_f^2)}{V^2\text{Im}\Sigma_f(\mu)}}
\]  \hspace{1cm} (4.23)

Without a proper imaginary part self energy \( \text{Im}\Sigma_f(\mu) \) from the strong correlations, \( \delta_c \) would dominate the denominator, and the Seebeck coefficient \( S' \) would be small in this case.

The Seebeck coefficient is found to have two maximum for some rare-earth compounds. Usually it is explained by the crystal field. Our theory shows another possibility. We know \( \bar{\epsilon}_f \) is roughly a constant at low temperature and increases rapidly at higher temperature, as shown in Fig. 5. of ref([58]). Based on equation (4.18), if \( \bar{\epsilon}_f \) has two intercepts with \( z^{-1}\pi K_B T / \sqrt{3} \), then the Seebeck coefficient should have two maximums.

### 4.3.3 The onset temperature for the coherence of \( f \) electrons

For the heavy Fermion system, the temperature \( T_o \) corresponding to the maximum of the resistivity is usually considered to be the onset temperature for the the coherence of \( f \) electrons. According to equation (4.19), \( \bar{\epsilon}_f \) should be of the order \( \text{Im}\Sigma_f(\mu) \) at \( T_o \). This means that the many body effect kicks in around \( T_o \) and positions \( \bar{\epsilon}_f \) at a value close to the chemical potential \( \mu \). Based on this fact, \( T_o \) should be of the same order as the Kondo temperature \( T_K \).

We propose that an estimated value for \( T_K \) should be \( 0.1 T_0 \). This is based on following facts. The DMFT calculation shows that \( T_0 \) is roughly \( 5 \sim 10 T_K [58] \). It was recently proposed that the density of states for the Kondo Liquid should be
Figure 4.3. The magnetic susceptibility of SIAM is fitted with the formulas for the density of states of Kondo liquid. The $T_0$ is around $8T_K$ in the fitting.

given by[88]:

$$\rho_{KL} = (1 - \frac{T}{T_0})^{3/2}(1 + \ln \frac{T_0}{T})$$

(4.24)

In DMFT, the temperature dependence of the magnetic susceptibility of the PAM is the same as that of its corresponding effective SIAM. Because of the scaling of SIAM, the magnetic susceptibility can be approximated by the universal curve for the magnetic susceptibility of the SIAM [26]. The universal curve for the magnetic susceptibility of the SIAM can be fitted with above formula to determine the relationship between $T_0$ and $T_K$. This fitting is shown in Fig.4.3. We find $T_0$ to be $8T_K$, which agrees with our proposal. We believe this is a reasonable estimation of $T_K$. With our proposal, the dense Kondo systems has a Kondo temperature of just a couple times larger than that of the dilute limit. This is a reasonable increase of Kondo temperature for the dense Kondo systems.
4.4 Conclusion

Some analytic results for the temperature variations of the resistivity and Seebeck coefficient have been derived for the periodic Anderson model. These results show good agreements with the experiment data of rare-earth compounds in the literature. The conditions for attaining large Seebeck coefficients are explored. We further propose that the Kondo temperature of the dense Kondo system to be 0.1 of the temperature corresponding to the maximum of the resistivity.
The effective Seebeck coefficient for semiconductors

A.1 introduction

The Seebeck effect, Peltier effect and Thomson effect have been discovered for more than 100 years. And the theory concerning these effects have been established[1, 2]. Based on these effects, solid state refrigerators have been developed[3]. There is a subtleness in the definition of Seebeck coefficient. This subtleness lies in the inequivalent definitions of phenomenal Seebeck coefficient and theoretical Seebeck coefficient. The detail of definitions are given in the first chapter. This subtleness needs to be addressed to get the right coefficient for the transfer of heat in solid state refrigerators.

The other motivation of this appendix is to explain the importance of the junctions between the thermoelectric material and cold reservoirs for solid state refrigerators. The junction is important because of Peltier effect. Or in other words, the elec-
trons from cold reservoirs have to thermally excited to get into the thermoelectric material. They will absorb heat from heat reservoirs during this process, which cools down the reservoirs. This appendix gives a clear explanation of the role of the junctions.

A.2 Seebeck coefficient

Start from the Boltzmann equation. In steady phenomena, we neglect the time dependence of the distribution function, and have the following equations:

\begin{equation}
0 = \nabla_r f \cdot v + \frac{1}{\hbar} \nabla_k f \cdot (e\vec{E} + ev \times \vec{B}) + \left(\frac{\partial f}{\partial t}\right)_s
\end{equation}

\begin{equation}
\approx \nabla_r f^{(0)} \cdot v + \frac{1}{\hbar} \nabla_k f^{(0)} \cdot (e\vec{E} + ev \times \vec{B}) + \left(\frac{\partial f}{\partial t}\right)_s
\end{equation}

\begin{equation}
f^{(0)} = \begin{cases} 
\frac{1}{e^{\beta(r)\xi} + 1} = \frac{1}{e^{\beta(r)\xi} + 1}, \\
e^{-\beta(r)\xi}, \\
\end{cases}
\end{equation}

for Fermi distribution,

for Boltzmann distribution.

\begin{equation}
\nabla_r f^{(0)} = (\nabla_r \mu(r) + \frac{\xi}{T} \nabla_r T)(-\frac{df^{(0)}}{d\xi})
\end{equation}

\begin{equation}
\nabla_k f^{(0)} = \hbar \nu_k \frac{df^{(0)}}{d\xi}
\end{equation}

\(e\) is the charge of charge carrier. For electron, it is a negative value. \(\mu\) is the chemical potential. It is easy to notice that most of equations are the same for Fermi distribution and Boltzmann distribution. Now we concentrate on the zero
magnetic field case. We can regroup these equations in following way:

\[ 0 = \mathbf{v}_k \cdot \left( -e\mathbf{E} + \nabla_r \mu(r) + \frac{\xi}{T} \nabla_r T \right) \left( -\frac{df^{(0)}}{d\xi} \right) + \left( \frac{\partial f}{\partial t} \right)_s \]  
\[ = \mathbf{v}_k \cdot \left( \nabla_r \mu(r) + \frac{\xi}{T} \nabla_r T \right) \left( -\frac{df^{(0)}}{d\xi} \right) + \left( \frac{\partial f}{\partial t} \right)_s \]  
\[ \bar{\mu} = \mu + e\phi \]  

\( \bar{\mu} \) is the electrochemical potential. Apply the relaxation time approximation,

\[ \left( \frac{\partial f}{\partial t} \right)_s = \frac{f - f^{(0)}}{\tau_t(\xi_k)} = \frac{\delta f}{\tau_t(\xi_k)} \]  

We arrived at equations for electric current, heat current and energy current:

\[ \mathbf{J} = 2e \int \frac{d^3k}{(2\pi)^3} \mathbf{v}_k \delta f(k) \]  
\[ = -\sigma \left( \nabla_r \mu \right) + b \nabla_r T \]  
\[ \sigma = 2e^2 \int \frac{d^3k}{(2\pi)^3} \tau_t(k) \mathbf{v}_k \mathbf{v}_k \left( -\frac{df^{(0)}}{d\xi} \right) \]  
\[ b = \frac{2e}{\sigma} \int \frac{d^3k}{(2\pi)^3} \tau_t(k) \mathbf{v}_k \mathbf{v}_k \xi \left( -\frac{df^{(0)}}{d\xi} \right) \]  
\[ \mathbf{J}_Q = 2 \int \frac{d^3k}{(2\pi)^3} \mathbf{v}_k \delta f(k) \xi \]  
\[ = \frac{\sigma bT}{e} \nabla_r \mu \]  
\[ = -2 \int \frac{d^3k}{(2\pi)^3} \tau_t(k) \mathbf{v}_k \mathbf{v}_k \xi \left( -\frac{df^{(0)}}{d\xi} \right) \nabla_r T \]  
\[ = \frac{\sigma bT}{e} \nabla_r \mu - K' \nabla_r T \]  
\[ \mathbf{J}_E = 2 \int \frac{d^3k}{(2\pi)^3} \mathbf{v}_k \delta f(k)(\epsilon + e\phi) \]  
\[ = \mathbf{J}_Q + \bar{\mu} \mathbf{J} \]
The driving forces for current are potential gradient, temperature gradient and charge density gradient. We can express the current in explicitly dependent of these three driving forces.

\[
\vec{J} = -\sigma \vec{V}_\phi - \frac{\sigma}{e} \left( \frac{\partial \mu}{\partial n} \right)_T \vec{V}_n \\
-\frac{\sigma}{e} \left( \frac{\partial \mu}{\partial T} \right)_n \vec{V}_n - \sigma \vec{V}_e T \\
= -\sigma \vec{V}_\phi - \sigma \vec{S} \vec{V}_n T - \frac{\sigma}{e} \left( \frac{\partial \mu}{\partial n} \right)_T \vec{V}_n \\
\overline{S} = b + \frac{1}{e} \left( \frac{\partial \mu}{\partial T} \right)_n
\]  

(A.19) 

(A.20) 

(A.21)

It is obvious from equation (A.20) that \( \sigma \) is the electric conductivity and \( \overline{S} \) is the theoretical Seebeck coefficient defined in section one. \( \overline{S} \) is also the effective Seebeck coefficient defined in Mahan’s paper[89], which takes account of all the effects of temperature gradient. \( b \) is the phenomenal Seebeck coefficient \( S \). The voltage across a conductor is equal to \( \Delta \bar{\mu}/e \), not the \( \int \vec{E} d\vec{l} \). (An example is the pn junction. When the applied voltage across the junction is zero, then \( \int \vec{E} d\vec{l} \) is obvious nonzero due to the electric field.) The voltmeter measures the difference of electrochemical potential. Setting \( \vec{J} = 0 \) in equation (A.11), we find \( V = \Delta \bar{\mu}/e = b \Delta T \). Compared with definition in equation (1.1), it is obvious that \( b \) is the phenomenal Seebeck coefficient \( S \). The theoretical Seebeck coefficient is a description of effective electric field generated by temperature gradient. While the phenomenal Seebeck coefficient is a description of voltage generated by temperature gradient. It is surprising that they are not in proportion to each other. The equation (A.21) is the relation between these two Seebeck coefficients.
Apply above equations for a homogeneous doped semiconductor. we have:

\[ \mathbf{J} = -\frac{n e^2 \tau_t}{m} \nabla \mu - \frac{k_B e \tau_t n}{m} \left( \frac{5}{2} - \mu \beta \right) \nabla r T \]  
(A.22)

\[ S = \frac{k_B}{e} \left( \frac{5}{2} - \mu \beta \right) \]
(A.23)

\[ = \frac{k_B}{e} \left( \frac{5}{2} - \log \frac{n}{N_c} \right) \]  
(A.24)

\[ N_c = \frac{2 (m \hbar^2 \pi \beta)^{3/2}}{e} \]  
(A.25)

\[ \overline{S} = S + \frac{1}{e} \left( \frac{\partial \mu}{\partial T} \right)_n = \frac{k_B}{e} \]  
(A.26)

The phenomenal Seebeck coefficient is the one actually measured. As the measurement of Seebeck coefficient just follows the phenomenal definition[1]. It is obvious that the phenomenal Seebeck coefficient decreases linearly with \( \log n \). This agrees with experiment results[3]. The surprising result to find is that \( \overline{S} \) is an universal constant. For a given temperature gradient, the electric field induced inside a homogeneous doped semiconductor is the same for different materials. This makes sense because for a close loop made by semiconductors, the current is solely driven by temperature gradient. Loop integrate of electric field should be zero. This probably is valid even for inhomogeneous doped semiconductors. As people are interested in inhomogeneous doping to increase the efficiency of refrigerator[90], \( \overline{S} \) may be an useful term in such kind of discussion. \( \overline{S} \) is a useful term for the calculation of electric field inside a material, which is necessary to find the modification of carrier density through Poisson’s equation. An example to use this term is by Mahan[89], who finds the modification of charge carrier density due to the present of current. But the modification is small, which means we can use the same carrier density without current for coefficients calculation.
A.3 refrigerator

Now let’s apply above equations to discuss the principle of refrigeration. A solid state refrigerator is made of two thermal reservoirs with a thermoelectric material sandwiched between them. If we just concentrate on the thermoelectric material, we can use the equation from (A.11)-(A.18) to work out the heat flow from the cold reservoir. One of the basic equation derived from equation (A.11) and (A.18) is:

\[ \vec{J}_Q = S T \vec{J} - K \nabla T \]  \hspace{1cm} (A.27)

The thing worth emphasizing is that the \( S \) is the phenomenal Seebeck coefficient and \( K \) is the thermal conductivity. So we can use direct experimental values of the Seebeck coefficients for efficiency calculation. The other details are worked out in Mahan’s review paper[3]. The basic answers are provided: for two thermal reservoirs with temperature \( T_c \) and \( T_h \), and thermoelectric material with a length of \( L \), the heat current from the cold source is:

\[ \vec{J}_Q = S T_c J - K \Delta T / L - J^2 L / (2\sigma) \]  \hspace{1cm} (A.28)

The efficiency is:

\[ \eta(J) = \frac{J_Q}{J V_a} = \frac{S T_c J - K \Delta T / L - J^2 L / (2\sigma)}{J^2 / \sigma + S J \Delta T} \]  \hspace{1cm} (A.29)

Now we include the junction between the thermal reservoirs and thermoelectric
material into our discussion. For simplicity, we assure that the reservoirs are made of metal, which have a neglectable Seebeck coefficient compared with semiconductor. The electrons in metals need to absorb some extra energy to pass into the semiconductor. This is called the Peltier effect. The energy absorbed is $e\Pi[91]$.

Based on Kelvin relations, we have:

$$\Pi = ST_c$$

We have two ways to get the efficiency of the solid state refrigerator with junctions. One is through considering the energy input and output for the reservoir regardless the inner structure. The net energy taken away from a reservoir is equal to the difference of output energy and input energy. For the process that happens near the cold reservoir, the temperature is a constant. Then the electrochemical potential $\mu$ is a constant. From equation (A.18), the energy taken away from the cold source is now just equal to the difference of output heat and input heat, as $\mu J$ cancels. We limit ourself to the situation that the current input is made of metal with small contact areas with the reservoirs. It is obvious that this is the best efficiency we can get. Then the heat input and voltage drop across the metal wire reservoir junction can be neglect. The efficiency is just $\frac{JQ}{\eta}$ as equation (A.29). We get the same result for efficiency as without considering junction!

We can find the efficiency in an alternate way. And the importance of junctions is demonstrated. This is also the best explanation of the principal of solid state refrigerator we can give. Due to the Peltier effect, the junction acts as a machine that loads every charge carrier with some extra heat when they are passing through[91]. During this process the heat is absorbed form the cold reservoir, and therefore cools down the cold reservoir. This process is solely responsible for the
cooling. The heat flow is continuous in the thermoelectric material, as the water flow in a channel. This heat flow does not take away any extra heat from its surroundings, as the water flow in the channel does not need extra sources around to sustain the flow. Then the heat taken away from the cold reservoir is just $JST_c$ due to Peltier effect. The heat input is through the thermal conduct, which is equal to $K \frac{dT}{dx}$. The same equation for voltage across the circuit applies. We arrive at the same result as above. *From this argument, it is obvious the efficiency does depend on the thermionic phenomena of the junction.* Nevertheless we can calculate the efficiency in a way that we do not explicitly mention the presence of junctions. This is because the heat flow is continuous in the thermoelectric material.

**A.4 conclusion**

The conclusion we arrived is: a) The phenomenal and theoretical definition of Seebeck coefficient are not equivalent. The phenomenal Seebeck coefficient is the one directly measured. The effective Seebeck coefficient is also an interesting and useful term. In homogeneous semiconductor, the effective Seebeck coefficient is a universal constant, which imply that the electric field induced by temperature gradient is independent of doping. b) The junctions of reservoirs with thermoelectric materials contribute to the efficiency of refrigerators. But we can find the efficiency without explicitly considering of the junction. And the previous results and the standards set for refrigerator materials are not changed.
The basic of dynamic mean field theory

B.1 The basic theory

The dynamic mean field theory is a non-perturbative theory. For a strong correlated lattice problem, we can single out a correlated site and introduce a non-interacting effective bath to describe the media which this correlated site couples to. The correlated site is then described by a single impurity Anderson model, which is given by following Hamiltonian:

\[ H = H_{corr} + H_{bath} + H_{coup} \]  
\[ H_{corr} = \sum_\sigma (\epsilon_f f_\sigma^\dagger f_\sigma + U f_\sigma^\dagger f_\sigma^\dagger f_{-\sigma} - f_{\sigma}^\dagger f_{-\sigma}) \]  
\[ H_{bath} = \sum_{k,\sigma} \epsilon_k C_k^\dagger C_k \]  
\[ H_{coup} = \sum_{k,\sigma} V_k (f_{k\sigma}^\dagger C_k + H.c) \]
where $H_{\text{corr}}$ describes the correlated site. $f_{k\sigma}$ ($f_{k\sigma}^\dagger$) destroys (creates) an electron with binding energy $\epsilon_f$ in the correlated site. $H_{\text{bath}}$ describes the effective media. $C_{k\sigma}$ ($C_{k\sigma}^\dagger$) destroys (creates) an electron with energy $\epsilon_k$ in the effective media. $H_{\text{coup}}$ describes the coupling between the correlated site and the effective media. The Green’s function for the correlated site is given by:

$$G(\omega) = \frac{1}{\omega - \epsilon_f - \Sigma_f - \Delta(\omega)} \quad (B.5)$$

$$\Delta(\omega) = \sum_k \frac{V_k^2}{\omega - \epsilon_k} \quad (B.6)$$

$\Sigma_f$ is the self energy introduced by the on-site correlation. $\Delta(\omega)$ is the hybridization function. Based on numerical renormalization group[92], which can also be shown with action of the single impurity Anderson model[51], the parameters of the effective bath enters the problem only through this hybridization function. We just need to determine this hybridization function for the effective media. The lattice Green’s functions of the lattice problem can be expressed as:

$$G_{kf}(\omega) = \frac{1}{\omega - \epsilon_f - \Sigma_f(k) - \xi_k} \quad (B.7)$$

where $G_{kf}^0 = 1/(\omega - \epsilon_f - \xi_k)$ is the Green’s function without on-site correlation $U$. $\Sigma_f(k)$ is the self energy introduced to describe the on-site correlation. The key approximation of the dynamic mean field theory is to replace $\Sigma_f(k)$ in the lattice Green’s function by $\Sigma_f$ of the correlated site’s Green’s function[93]. By definition, the lattice Green’s function is related with the correlated site’s Green’s function.
by:

\[ G(\omega) = \frac{1}{N} \sum_k G_{kf}(\omega). \]  

(B.8)

where \( N \) is the number of the correlated sites. This is the self-consistency equation of the dynamic mean field theory. With above equation, we can determine the hybridization function of the effective bath. Above equations is a complete set, which can be solved self-consistently to obtain the Green’s functions. The transport properties of the problem can be expressed as current-current correlation function, which can be calculated with above Green’s functions. So dynamic mean field theory provides a solution to the lattice problem.

### B.2 The infinite dimension limit

The dynamic mean field theory is exact in some limits[93]. Two of them are trivial. One is the non-interacting limit where the on-site correlation \( U \) is zero. The other is the atomic limit where the coupling of the correlated sites to other sites is zero. The most interesting and non-trivial limit is the infinite dimension limit. We prove this statement here. We show the equation \( \Sigma_f(k) = \Sigma_f(\omega) \) we used in the dynamic mean field is an exact relation instead of an approximation in the infinite dimension limit.

We use the perturbation theory to prove above statement[72]. We limit ourself to the second order perturbation theory. Higher order perturbations can be carried out in a similar way and does not change the results. From the perturbation theory
in Chapter 2, we can write down the self energy of the lattice Green’s function as:

\[ \Sigma_f(k) = \frac{U^2}{N^2 \beta^2} \sum_{p,q,iq,ip} G_f(k + q, ik_n + iq) G_f(p, ip) G_f(p + q, ip + iq) \] (B.9)

where \( G_f(k, ik) \) is the Hatree-Fock lattice Green’s function. The Hatree-Fock site Green’s function are given by:

\[ G_{ij}(ik_n) = \frac{1}{N} \sum_k e^{ik(R_i - R_j)} G(k, ik_n) \] (B.10)

where \( R_i \) is the position of \( i \) site. The self energy in the site representation is given by:

\[ \Sigma_{ij}(ik_n) = \frac{1}{N} \sum_k e^{ik(R_i - R_j) \Sigma_f(k)} = \frac{U^2}{N^2 \beta^2} \sum_{iq,ip} G_{ij}(ik_n + iq) G_{ij}(ip) G_{ji}(ip + iq) \] (B.11)

The effective coupling between two nearest correlated sites is denoted as \( t \). In infinite dimension, this coupling must scales with \( 1/d^\gamma \) with \( \gamma \geq 1/2 \) to have a non-trivial density of states and other physical quantities. (\( d \) is the dimension.) The \( G_{ij} \) connecting sites \( i \) and \( j \) involves a factor \( t^{|i-j|} \). Based on above equation, \( \Sigma_{ij} \) has a factor \( t^{3|i-j|} \). The number of sites at distance \( |i - j| \) is proportional to \( d^{|i-j|} \). For a particular \( i \), summation of \( j \) at a particular distance \( |i - j| \) results in a factor of \( d^{|i-j|} t^{3|i-j|} = d^{(2-3\gamma)|i-j|} \). In the infinite dimension limit, the limit of
above summation is zero. Then we have:

\[ \Sigma_f(k) = \frac{1}{N} \sum_{ij} e^{-ik(R_i - R_j)} \Sigma_{ij} = \frac{1}{N} \sum_i \Sigma_{ii} = \Sigma_{ii} \] (B.12)

This proves the equation we used in the dynamic mean field theory. This result shows the local nature of the perturbation theory in the infinite dimension. Further discussion can be found in Georges’s review paper[51].
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