



# Strong Electron-Phonon Interaction and Colossal Magnetoresistance in $\text{EuTiO}_3$

Chen Ruofan

A0112308W

**Supervisor:**

Professor Wang Jian-Sheng

**Examiners:**

Doctor Pereira, Vitor Manuel

Associate Professor Adam, Shaffique

Professor Zhiping Yin

Thesis submitted for the degree of  
Doctor of Philosophy, Department of Physics  
National University of Singapore

2017



## Declaration

I hereby declare that this thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information, which have been used in the thesis. This thesis has also not been submitted for any degree in any university previously.

*Chen Ruofan*

---

Chen Ruofan

25 July 2017



## **Acknowledgements**

I would like to express my special gratitude to my supervisor Prof. Wang Jian-Sheng. His patient guidance has benefited me a lot. His serious scientific attitude and rigorous scholarship makes me stand on a firm ground.

I would also like to thank my colleagues and friends for helpful discussions and literature recommendations.

Finally I would like express my thanks to my family for their support and encouragement.



# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
<b>2</b>	<b>Transport Theories for Electrons</b>	<b>5</b>
2.1	Diffusion Phenomena . . . . .	5
2.2	Drude Theory . . . . .	9
2.3	Fermi's Golden Rule . . . . .	12
2.4	Boltzmann Equation . . . . .	16
2.5	The Generalized Susceptibility . . . . .	23
2.6	The Fluctuation-Dissipation Theorem . . . . .	27
2.7	The Kubo-Greenwood Formula . . . . .	33
2.8	The Green-Kubo Formula . . . . .	37
2.9	The Green-Kubo Formula for Electrical Conductivity . . . . .	41
2.10	Non-Equilibrium Green's Function Formalism . . . . .	48
2.11	Fluctuations . . . . .	55
2.12	Onsager's Principle . . . . .	59
2.13	The Green-Kubo Formula for Heat Conductivity . . . . .	68
<b>3</b>	<b>Dynamical Mean-Field Theory</b>	<b>73</b>
3.1	Anderson Impurity Model . . . . .	73
3.2	The Basic Procedures of the Dynamical Mean-Field Theory . . . . .	79
3.3	The Dynamical Mean-Field Theory with Constant Filling . . . . .	83
3.4	Boson Coherent States . . . . .	85
3.5	Fermion Coherent States . . . . .	88

3.6	Gaussian Integrals for Coherent States . . . . .	94
3.7	Coherent State Functional Integral Formalism . . . . .	97
3.8	Linked Cluster Theorem . . . . .	103
3.9	Derivation of the Dynamical Mean-Field Equations . . . . .	107
<b>4</b>	<b>Dynamical Mean-Field Theory for Small Polaron</b>	<b>113</b>
4.1	Impurity Model at Zero Temperature . . . . .	113
4.2	The Impurity Solver for the Holstein Model: Zero Temperature Formalism . . . . .	115
4.3	The Impurity Solver for Holstein Model: Finite Temperature Formalism . . . . .	119
4.4	Dynamical Mean-Field Equations . . . . .	121
<b>5</b>	<b>Strong Electron-Phonon Interaction and Colossal Magnetoresistance in <math>\text{EuTiO}_3</math></b>	<b>123</b>
5.1	Magnetoresistance . . . . .	123
5.2	Magnetization of $\text{EuTiO}_3$ . . . . .	126
5.3	Colossal Magnetoresistance in $\text{EuTiO}_3$ . . . . .	130
5.4	Strong Electron-Phonon Interaction in $\text{EuTiO}_3$ . . . . .	135
5.5	Strong Electron-Phonon Interaction and Colossal Magnetoresistance in $\text{EuTiO}_3$ . . .	137
5.6	Results and Discussions . . . . .	143
<b>6</b>	<b>Summary</b>	<b>145</b>
	<b>Bibliography</b>	<b>147</b>



# List of Figures

2.1	Integration contour for $\frac{\alpha(\omega)}{\omega-\omega_0}$ . . . . .	26
3.1	Basic dynamical mean-field theory loop. . . . .	82
3.2	The density of states before and after the dynamical mean-field theory calculation. . . . .	84
3.3	The loop for dynamical mean-field theory with constant filling. . . . .	85
5.1	Schematic diagram for double exchange mechanism. . . . .	124
5.2	A. J. Millis, Nature, <b>392</b> , 147 (1998) . . . . .	125
5.3	The localized spin model for EuTiO <sub>3</sub> . . . . .	126
5.4	Experimental data (dots) and Mean-Field calculation (solid lines) of magnetization for EuTiO <sub>3</sub> with different temperature and magnetic field. The experimental data are provided by Km Rubi and Prof. Mahendiran. . . . .	128
5.5	Experimental resistivities and mean-field calculation of magnetization of EuTiO <sub>3</sub> . . . . .	131
5.6	Schematic depiction of the EuTiO <sub>3</sub> model . . . . .	132
5.7	Resistivity without magnetic field. A function $y = e^{152.53/x+6.66}$ is used to fit the experimental resistivity, where $y = \rho/(\Omega \cdot \text{cm})$ and $x = T/\text{K}$ . . . . .	134
5.8	Simple fitting resistivities (lines), and the experimental data (dots) are plotted here for comparison. . . . .	134

5.9	The density of states of $t_{2g}$ orbitals of Ti atom by a first principle calculation. The Fermi level, which needs to be fitted by experimental data later, is not specified here. The first principle density functional theory calculation is carried out within the spin-polarized generalized gradient approximation (GGA) [115] using norm-conserving pseudopotentials. We use a kinetic energy cutoff of 60 Ry and a $10 \times 10 \times 10$ $\Gamma$ -centered $k$ -point mesh for the unit cell simulations. Then the mesh is interpolated up to $40 \times 40 \times 40$ by Wannier functions [116, 117]. This calculation is done by Ji-Chang Ren. . . . .	138
5.10	The spectral density calculated by dynamical mean-field theory with $g =$ (a) 0.6 eV, (b) 0.8 eV, (c) 1.0 eV, (d) 1.2 eV, (e) 1.6 eV, and (f) 2.0 eV. . . . .	139
5.11	Resistivities of EuTiO <sub>3</sub> . Solid lines represent theoretical results, and experimental data (dots) are plotted here for comparison. . . . .	140
5.12	Density of states of the coupling constants between electronic states with localized LO mode phonon states. This calculation is done by Ji-Chang Ren. . . . .	142

# Chapter 1

## Introduction

The electrical resistivity of some materials changes in the presence of external magnetic field, and such phenomenon is called magnetoresistance effect. If the electrical resistivity of the materials changes dramatically then such magnetoresistance is called colossal magnetoresistance. The conventional magnetoresistance enables changes of resistivity up to a few percent, whereas the resistivity of materials featuring colossal magnetoresistance may change by orders of magnitude [1, 2].

In the past few decades most theoretical studies of colossal magnetoresistance focus on perovskite manganites [3–11]. The most commonly studied perovskite manganites have the chemical formula  $R_{1-x}A_xMnO_3$ , where R and A are trivalent rare earth (La or Pr for example) and divalent alkaline ions (Ca or Sr for instance) respectively. In such systems electrons fill the  $3d$  shell of the Mn. Ca and Sr act as hole dopants here, therefore when the system is doped there would be  $4 - x$  electrons, or  $x$  holes, in the  $3d$  shell of the Mn. These holes can hop from a Mn ion to another, but due to strong Hund coupling on a given Mn ion this hopping process is inhibited if the ionic spins of Mn ions are antiparallel, i.e., hopping is dependent on the relative orientation of the ionic spins. Such mechanism is called “double exchange” which was first proposed by Zener [12]. The effective Hamiltonian presenting double exchange mechanism is usually written in the form of the Hamiltonian of Kondo model [13, 14].

The early physical explanation of colossal magnetoresistance was based on double exchange mechanism. However, Millis *et al.* [3] pointed out that in  $La_{1-x}Sr_xMnO_3$  double exchange alone can not explain its resistivity, and Jahn-Teller effect must be taken into consideration. Later many

works [3–11] showed that strong electron-phonon interaction indeed plays an important role in colossal magnetoresistance.

Reports on magnetoresistance in rare earth titanates of formula  $\text{RTiO}_3$  are scarce because of their large resistivities at low temperature. Recently Km Rubi *et al.* [15, 16] found that the undoped perovskite titanium oxide  $\text{EuTiO}_3$  exhibits colossal magnetoresistance. At low temperatures,  $\text{EuTiO}_3$  has very large resistivity and exhibits colossal magnetoresistance: in the presence of external magnetic field its resistivity drops dramatically. Such phenomenon is hard to be explained without a good theory of strongly correlated systems.

When dealing with a strongly correlated system the dynamical mean-field theory is a powerful tool which enables us to obtain the electronic structure of the system via non-perturbative procedures. Once the electronic structure has been found, we can calculate the corresponding electrical transport coefficients via various transport theories.

We find that although the double exchange mechanism is irrelevant, the strong electron-phonon interaction also plays an important role in colossal magnetoresistance in  $\text{EuTiO}_3$ . In this thesis, based on the dynamical mean-field theory for small polaron we have calculated the transport properties of  $\text{EuTiO}_3$  and explained its colossal magnetoresistance.

This thesis is organized as follows:

- Chapter 2 gives a comprehensive review on transport theories of electron which can collaborate with dynamical mean-field theory. We focus on linear response theory, especially the derivation of Kubo-Greenwood formula which is most suitable for the electrical conductivity calculation using results obtained by the dynamical mean-field theory.
- Chapter 3 gives an introduction to the general procedures of the dynamical mean-field theory, and chapter 4 gives an introduction to the dynamical mean-field theory for small polaron. The latter one is the method adopted to calculate the electronic structure of  $\text{EuTiO}_3$  in this thesis.
- Chapter 5 gives the actual calculation of transport properties of  $\text{EuTiO}_3$ . We first introduce the magnetic properties of  $\text{EuTiO}_3$  which are of crucial importance to explain the colossal magnetoresistance. Then a simple fitting is given as an explanation. Such simple fitting reveals the fundamental reason of colossal magnetoresistance but fails to explain the high

resistivity of  $\text{EuTiO}_3$ . Finally based on the dynamical mean-field theory and linear response theory we calculate the electrical conductivity and explain the colossal magnetoresistance in  $\text{EuTiO}_3$ . The results reach a qualitative agreement with experimental data.

A word about the unit of temperature used in this thesis. In all subsequent formulas the temperature  $T$  is assumed to be, unless otherwise specified, measured in energy units. Accordingly, the entropy  $S$  is a dimensionless quantity. If the temperature is measured in Kelvin, then the substitutions below need to be made in all formulas:

$$T \rightarrow k_B T, \quad S \rightarrow S/k_B, \tag{1.1}$$

where  $k_B$  is the Boltzmann constant.



## Chapter 2

# Transport Theories for Electrons

The movement of electrons can induce electricity current and heat current. Since there would be no net current in complete equilibrium state, the net current is usually the response to an external electric field or temperature gradient. The corresponding response coefficients, such as electrical conductivity, are what we most concern in transport theories. In this chapter, we shall review various transport theories of electrons.

### 2.1 Diffusion Phenomena

When particles suspend in a fluid, they do random motion due to their collision with the environment such as other fast moving particles or random potentials [17]. This random motion is called *Brownian motion*, named after the botanist Robert Brown [18]. In 1905 Albert Einstein gave the first clear theoretical explanation of such phenomena and thus established the basic foundation of the atomic theory of matter [19]. The theory of Brownian motion was further developed by many others. The review of classical theory of Brownian motion can be found in Ref [20].

Now let us consider a medium which contains a large number of electrons, and suppose they are doing Brownian motion. Define particle density as  $n(\mathbf{r}, t)$ . Brownian motion would induce a net movement of electrons from a region of high concentration (or high chemical potential) to a region of low concentration (or low chemical potential), and make the distribution of electrons tend toward uniformity. Such a process is called *diffusion* [21, 22].

When the density distribution varies smoothly in space, the particle current density is expected

to be proportional to the gradient of the density distribution:

$$\mathbf{j} = -D\nabla n, \quad (2.1)$$

where  $\mathbf{j}$  is the particle current density and  $D$  is the *diffusion constant*. According to the equation of continuity

$$\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{j} = 0, \quad (2.2)$$

we find the equation of the rate of change of the density distribution:

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D\Delta n. \quad (2.3)$$

This is the *diffusion equation*.

The diffusion constant is related to the electrical conductivity. When there is an uniform electric field  $\mathbf{E}$ , the chemical potential  $\mu$  should be replaced by  $\mu - e\phi$ , where  $\phi = -\mathbf{E} \cdot \mathbf{r}$  is the electric potential and  $e$  is the positive electric charge (the electron has a charge of  $-e$ ). When electrons are non-degenerate, they obey Boltzmann distribution  $f(\varepsilon) = \exp[(\mu - \varepsilon)/T]$ . It should be emphasized that the *local equilibrium* is assumed here, which means that although the whole system is not in complete equilibrium so the intensive parameters like temperature or chemical potential can vary in space and time, any given point, along with its neighborhood, is in equilibrium. Let  $n_0$  denote the particle density of electrons with no electric field, then the particle density with a uniform electric field can be written as

$$n(\mathbf{r}) = n_0 e^{-e\phi/T} = n_0 e^{e\mathbf{E} \cdot \mathbf{r}/T}. \quad (2.4)$$

Substituting the above expression into equation (2.1) we obtain the formula for the particle current density of electrons

$$\mathbf{j} = -D\nabla n = -\frac{neD}{T}\mathbf{E}, \quad (2.5)$$

and the corresponding electricity current density

$$-e\mathbf{j} = \frac{ne^2D}{T}\mathbf{E}. \quad (2.6)$$



According to the definition of electrical conductivity  $\sigma$  we find that

$$\sigma = \frac{ne^2D}{T}, \quad (2.7)$$

and this formula shows that the electrical conductivity can be expressed by the diffusion constant.

In diffusion theory, there is another important quantity called *electrical mobility*, here we denote it by  $b$ , which is the ability of electrons to move through a medium in response to an electric field. According to its definition, when an electron is accelerated by uniform electric field, it would finally reach a constant drift velocity

$$-\mathbf{v} = b\mathbf{E}, \quad (2.8)$$

there is a minus sign before the velocity because the electron carries negative charge. Then the electricity current density can be expressed as

$$-e\mathbf{j} = -nev = neb\mathbf{E}, \quad (2.9)$$

and the electrical conductivity is then

$$\sigma = neb. \quad (2.10)$$

Comparing equation (2.7) with (2.10) we find that

$$b = \frac{eD}{T}, \quad (2.11)$$

and this formula is known as the *Einstein relation*.

The above diffusion theory states that if the diffusion constant or the electrical mobility is known, then electrical conductivity can be calculated through the above formulas. However, they are not easy to obtain. In the rest of this section we shall present the relation between the diffusion constant and Brownian motion.

Since Brownian motion is a stochastic process, the most important question is that if, a particle is at position  $\mathbf{r}_1$  at time  $t_1$ , what is the probability density of finding it at position  $\mathbf{r}_2$  at time  $t_2$  which succeeds  $t_1$ . Let  $P(\mathbf{r}_2, t_2 | \mathbf{r}_1, t_1)$  be defined as probability density of finding a particle at position  $\mathbf{r}_2$  at time  $t_2$  while this particle is at position  $\mathbf{r}_1$  at time  $t_1$ . This quantity is called

*transition probability.* According to this definition, the particle density  $n(\mathbf{r}, t)$  at position  $\mathbf{r}$  and at time  $t$  is

$$n(\mathbf{r}, t) = \int P(\mathbf{r}, t|\mathbf{r}_0, t_0)n(\mathbf{r}_0, t_0)d\mathcal{V}_0, \quad (2.12)$$

where  $n(\mathbf{r}_0, t_0)$  is the density at  $\mathbf{r}_0$  and  $t_0$ , and  $d\mathcal{V}_0$  is the infinitesimal volume element with respect to  $\mathbf{r}_0$ , in other words, the volume integration is over  $\mathbf{r}_0$ . Substituting this expression of  $n(\mathbf{r}, t)$  into the diffusion equation (2.3) we have

$$\frac{\partial}{\partial t} \left[ \int P(\mathbf{r}, t|\mathbf{r}_0, t_0)n(\mathbf{r}_0, t_0)d\mathcal{V}_0 \right] = D\Delta \left[ \int P(\mathbf{r}, t|\mathbf{r}_0, t_0)n(\mathbf{r}_0, t_0)d\mathcal{V}_0 \right], \quad (2.13)$$

or

$$\int \frac{\partial P(\mathbf{r}, t|\mathbf{r}_0, t_0)}{\partial t} n(\mathbf{r}_0, t_0)d\mathcal{V}_0 = D \int [\Delta P(\mathbf{r}, t|\mathbf{r}_0, t_0)] n(\mathbf{r}_0, t_0)d\mathcal{V}_0. \quad (2.14)$$

From the equation above we can see that if particle density  $n(\mathbf{r}, t)$  satisfies the diffusion equation then the transition probability also satisfies the diffusion equation:

$$\frac{\partial}{\partial t} P(\mathbf{r}, t|\mathbf{r}_0, t_0) = D\Delta P(\mathbf{r}, t|\mathbf{r}_0, t_0). \quad (2.15)$$

Because equation (2.15) must be satisfied for an arbitrary initial condition  $n(\mathbf{r}_0, t_0)$ , it can be simply written as

$$\frac{\partial}{\partial t} P(\mathbf{r}, t) = D\Delta P(\mathbf{r}, t). \quad (2.16)$$

The simplest transition probability  $P(\mathbf{r}, t|\mathbf{r}_0, t_0)$  is the solution of equation (2.15) with the initial condition that the particle is at  $\mathbf{r}_0$  at  $t_0$ :

$$P(\mathbf{r}, t_0|\mathbf{r}_0, t_0) = \delta(\mathbf{r} - \mathbf{r}_0), \quad (2.17)$$

and it is given by

$$P(\mathbf{r}, t|\mathbf{r}_0, t_0) = \left[ \frac{1}{\sqrt{4\pi D(t-t_0)}} \right]^d \exp \left[ -\frac{(\mathbf{r} - \mathbf{r}_0)^2}{4D(t-t_0)} \right], \quad (2.18)$$

where  $d$  is the dimension of the space. This is the simplest possible idealization of Brownian motion. It can be seen that the above formula is a Gaussian distribution in space, so let  $t_0 = 0$  and  $\mathbf{r}_0 = 0$

we have

$$\langle \mathbf{r}^2 \rangle(t) = \int \mathbf{r}^2 P(\mathbf{r}, t) d\mathcal{V} = 2dDt. \quad (2.19)$$

Therefore we reach an important conclusion that in Brownian motion the average of the square of displacement of a particle is proportional to time, and the coefficient is  $2dD$ . This provides a way to calculate the diffusion constant. For example, we can obtain the quantity  $\langle \mathbf{r}^2 \rangle(t)$  through a molecular dynamics simulation first, and then obtain the diffusion constant accordingly.

The gradient of temperature can also induce a net current. Let  $\rho(\varepsilon)$  denote the density of states, then the particle number density can be written as

$$n = \int \rho(\varepsilon) e^{(\mu-\varepsilon)/T} d\varepsilon, \quad (2.20)$$

where the temperature is a function of coordinates  $T(\mathbf{r})$  now. Hence the particle current density is

$$\mathbf{j} = -D\nabla n = -D \left[ \int \rho(\varepsilon) \frac{\varepsilon - \mu}{T} e^{(\mu-\varepsilon)/T} d\varepsilon \right] \frac{\nabla T}{T}, \quad (2.21)$$

denoting the integral in the square bracket by  $k_T$  then

$$\mathbf{j} = -Dk_T \frac{\nabla T}{T}, \quad (2.22)$$

where  $k_T$  is called the *thermal diffusion ratio* and  $Dk_T$  is called the *thermal diffusion constant*.

For heat current, there is an analog diffusion formula which is known as *Fourier's law*. It states that the heat current density  $\mathbf{j}_q$  is proportional to the gradient of the temperature:

$$\mathbf{j}_q = -k\nabla T, \quad (2.23)$$

where  $k$  is called the *thermal conductivity*.

## 2.2 Drude Theory

Drude theory is a phenomenological approach to calculate the electrical conductivity, which is based on Newton's second law of motion. It was introduced by Paul Drude in 1900 [23]. In the presence

of a static electric field there is a drift velocity  $\mathbf{v}$ , an acceleration force  $-e\mathbf{E}$  and a friction force  $-m^*\mathbf{v}/\tau$  for electrons, thus Newton's equation writes

$$m^* \frac{d\mathbf{v}}{dt} = -e\mathbf{E} - \frac{m^*\mathbf{v}}{\tau}. \quad (2.24)$$

Here  $m^*$  is the effective mass of an electron in the medium. The last term in equation (2.24) introduces a phenomenological *transport relaxation time*  $\tau$ , which accounts for the damping of the electron due to its interaction with the medium or other particles. When the acceleration and friction are balanced, i.e.  $-e\mathbf{E} - m^*\mathbf{v}/\tau = 0$ , we find the steady state velocity

$$\mathbf{v} = -\frac{e\mathbf{E}\tau}{m^*}. \quad (2.25)$$

Since the particle current density  $\mathbf{j}$  can be expressed as  $n\mathbf{v}$ , the electricity current density is

$$-e\mathbf{j} = \frac{ne^2\tau}{m^*}\mathbf{E}, \quad (2.26)$$

thus the electrical conductivity is just

$$\sigma = \frac{ne^2\tau}{m^*}. \quad (2.27)$$

Comparing this expression with equation (2.10) we reach a relation between the relaxation time and the electrical mobility:

$$b = \frac{e\tau}{m^*}. \quad (2.28)$$

Now assume the electric field is suddenly terminated at time  $t = t_0$ . Then for  $t > t_0$  the velocity would be decay exponentially:

$$\mathbf{v} = \mathbf{v}_0 e^{-(t-t_0)/\tau}. \quad (2.29)$$

Thus we see that the relaxation time gives the decay of the average velocity of electrons.

If the electric field is not static but varying with time, we can write down the Fourier components of equation (2.24) as

$$-i\omega m^* \mathbf{v}_\omega = -e\mathbf{E}_\omega - \frac{m^* \mathbf{v}_\omega}{\tau}, \quad (2.30)$$

the solution is

$$\mathbf{v}_\omega = -\frac{e\tau}{m^*(1-i\omega\tau)}\mathbf{E}_\omega, \quad (2.31)$$

and the corresponding electricity current density in frequency space is

$$-e\mathbf{j}_\omega = \frac{ne^2\tau}{m^*(1-i\omega\tau)}\mathbf{E}_\omega. \quad (2.32)$$

Thus we obtain the electrical conductivity as a function of frequency:

$$\sigma(\omega) = \frac{\sigma_0}{1-i\omega\tau}, \quad \sigma_0 = \frac{ne^2\tau}{m^*}. \quad (2.33)$$

This form of the electrical conductivity is called the *Drude formula*.

Because Drude theory is based on a classical theory, at first glance it should be invalid for electrons in solids where quantum mechanics must be involved. But in fact, the Drude formula is quite good in many cases. The reason is that although the Drude formula is derived from Newton's equation, its key parameters are determined by quantum effects of the system. The effective mass  $m^*$  is controlled by the band structure of electrons, and the relaxation time  $\tau$  is in principle determined by all transport processes. Besides, the Drude formula can be derived from Boltzmann equation, this is also one of the reasons why it is accurate enough in many cases.

The ultimate reason why Drude theory works so well was established by Lev Landau with the *Fermi liquid* theory [24, 25]. Fermi liquid describes the *elementary excitations* of the interacting electronic system by weak coupled *quasi particles*. Thus we can understand the electron in Drude theory as not a real particle but an elementary excitation.

The transport relaxation time  $\tau$  is the fundamental quantity in the Drude formula. Here we shall present the relationship between  $\tau$  and the retarded Green's function. Once the energy dependent retarded Green's function  $G^R(E)$  (the  $\mathbf{k}$  dependence of the Green's function is not considered here) is obtained, the corresponding self-energy  $\Sigma^R(E)$  is automatically known. The energy  $E$  of an electron state then should be replaced by  $E + \Sigma^R$ . According to the general statement of quantum mechanics, the time evolution phase factor of a definite energy state is  $e^{-\frac{i}{\hbar}Et}$ , in other words, the

time dependent wave function  $\Psi(t)$  is written as

$$\Psi(t) = \psi e^{-\frac{i}{\hbar}Et}, \quad (2.34)$$

where  $\psi$  is a function with no time dependence. Since  $\Sigma^R$  is the self-energy of the retarded Green's function,  $\text{Im } \Sigma^R$  is a negative quantity. Replace  $E$  by  $E + \Sigma^R$  and the wave function becomes

$$\Psi(t) = \psi e^{-\frac{i}{\hbar}(E+\Sigma^R)t} = \psi e^{-\frac{i}{\hbar}(E+\text{Re } \Sigma^R)t} e^{\frac{1}{\hbar} \text{Im } \Sigma^R t}. \quad (2.35)$$

The square modulus of this wave function is

$$|\Psi(t)|^2 = |\psi|^2 e^{\frac{2}{\hbar} \text{Im } \Sigma^R t}, \quad (2.36)$$

and there is an exponential decay in this expression. Comparing this decay factor with the damping factor expressed by relaxation time  $e^{-t/\tau}$  we find that

$$\tau(E) = -\frac{\hbar}{2 \text{Im } \Sigma^R(E)}. \quad (2.37)$$

The relaxation time calculated in this way is energy dependent, and in a metal, the values around the Fermi energy  $E_F$  are most important. Therefore the Drude formula in a metal can be written as

$$\sigma(\omega) = \frac{ne^2\tau(E_F)}{[1 - i\omega\tau(E_F)]m^*}, \quad (2.38)$$

where  $n$  is the corresponding carrier density.

The formulas above enable us to calculate the relaxation time via the retarded Green's function. The Green's function of electrons can be calculated approximately in many ways such as the perturbative expansion, the coherent potential approximation and the dynamical mean field theory.

## 2.3 Fermi's Golden Rule

In this section we shall derive a simple but important formula for the transition rate from one energy eigenstate into other energy eigenstates under a perturbation. It is usually called *Fermi's golden*

rule, which is named after Enrico Fermi [26]. Although named after Fermi, most work leading to this formula is due to Paul Dirac [27]. This formula is the basis of all linear approximations in quantum mechanics, such as linear response theory. It also appears in the Boltzmann equation approach for electron transport as providing an useful approximation.

Let us first introduce the time dependent perturbation theory developed by Paul Dirac [28]. Consider an unperturbed system of a given time independent Hamiltonian  $\hat{H}_0$  and energy eigenstates  $\Psi_k^{(0)}$  with corresponding eigenenergies  $E_k^{(0)}$ . If there is a time dependent perturbation  $\hat{V}(t)$ , the Hamiltonian becomes

$$\hat{H} = \hat{H}_0 + \hat{V}(t), \quad (2.39)$$

and the corresponding equation of the wave functions  $\Psi(t)$  is

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = [\hat{H}_0 + \hat{V}(t)]\Psi(t). \quad (2.40)$$

We shall now seek the solution of the perturbed system in the form of a combination of unperturbed wave functions  $\Psi_k^{(0)}$  as

$$\Psi(t) = \sum_k a_k(t) \Psi_k^{(0)}(t), \quad (2.41)$$

where the expansion coefficients  $a_k(t)$  are functions of time. Substituting (2.41) into (2.40) and recalling that the function  $\Psi_k^{(0)}$  satisfies the equation

$$i\hbar \frac{\partial \Psi_k^{(0)}}{\partial t} = \hat{H}_0 \Psi_k^{(0)} = E_k^{(0)} \Psi_k^{(0)}, \quad (2.42)$$

we have

$$i\hbar \sum_k \Psi_k^{(0)}(t) \frac{da_k(t)}{dt} = \sum_k a_k(t) \hat{V}(t) \Psi_k^{(0)}(t). \quad (2.43)$$

Multiplying both sides of this equation on the left by  $\Psi_m^{(0)*}$  and integrating over the space we obtain

$$i\hbar \frac{da_m(t)}{dt} = \sum_k V_{mk}(t) a_k(t), \quad (2.44)$$

where

$$V_{mk}(t) = \langle m | \hat{V}(t) | k \rangle e^{i\omega_{mk}t} = V_{mk} e^{i\omega_{mk}t}, \quad \omega_{mk} = \frac{E_m^{(0)} - E_k^{(0)}}{\hbar}, \quad (2.45)$$

are the matrix elements of the perturbation. Note that  $V_{mk} = \langle m | \hat{V}(t) | k \rangle$  are also functions of time.

Let the unperturbed wave function be the wave function of the  $n$ th stationary state  $\Psi_n^{(0)}$ , then the corresponding values of the coefficients in zeroth order approximation are  $a_n^{(0)} = 1$  and  $a_k^{(0)} = 0$  for  $k \neq n$ . We seek the solution of first order approximation of  $a_k$  in the form  $a_k = a_k^{(0)} + a_k^{(1)}$ . Substituting  $a_k = a_k^{(0)} + a_k^{(1)}$  on the left side of (2.44) and substituting  $a_k = a_k^{(0)}$  on the right side of (2.44) which already contains the small quantities  $V_{mk}$  gives

$$i\hbar \frac{da_k^{(1)}(t)}{dt} = V_{kn}(t). \quad (2.46)$$

Integrating this equation with respect to time gives

$$a_k^{(1)} = -\frac{i}{\hbar} \int V_{kn}(t) dt = -\frac{i}{\hbar} \int V_{kn} e^{i\omega_{kn}t} dt. \quad (2.47)$$

The squared modulus of  $a_k^{(1)}$  determines the probability for the system to be in the  $k$ th state perturbed from  $n$ th unperturbed state. By convention, when transition probabilities are discussed we denote the initial state by  $i$  and the final state by  $f$ , and denote  $a_f^{(1)}$ , which is the first order coefficient perturbed from  $i$ th unperturbed state, by simply  $a_{fi}$ . And the corresponding unperturbed energy  $E_i^{(0)}$  and  $E_f^{(0)}$  are denoted by just  $E_i$  and  $E_f$ .

Let us focus on one Fourier component of the perturbation  $\hat{V}(t)$ , in other words, suppose the perturbation operator is<sup>1</sup>

$$\hat{V}(t) = \hat{V} e^{-i\omega t}. \quad (2.48)$$

Assuming the perturbation starts at time  $t = 0$ , then we have

$$a_{fi} = -\frac{i}{\hbar} \int_0^t V_{fi}(\tau) d\tau = -V_{fi} \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\hbar(\omega_{fi} - \omega)}. \quad (2.49)$$

Therefore the squared modulus of  $a_{fi}$  is just

$$|a_{fi}|^2 = |V_{fi}|^2 \frac{4 \sin^2[\frac{1}{2}(\omega_{fi} - \omega)t]}{\hbar^2(\omega_{fi} - \omega)^2}, \quad (2.50)$$

---

<sup>1</sup>Note that the perturbation operator written in this way is not Hermitian, therefore it does not correspond to a real perturbation. A real periodic perturbation operator with frequency  $\omega$  may be written as  $\hat{V}(t) = \hat{V} e^{-i\omega t} + \hat{V}^\dagger e^{i\omega t}$ .



and noticing that when  $t$  goes to infinity  $\lim_{t \rightarrow \infty} \frac{\sin^2 \alpha t}{\pi t \alpha^2} = \delta(\alpha)$ , then we have

$$|a_{fi}|^2 = \frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_f - E_i - \hbar\omega)t. \quad (2.51)$$

Thus the probability transition rate from initial state  $i$  to final state  $f$  per unit time is

$$w_{fi} = \frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_f - E_i - \hbar\omega). \quad (2.52)$$

This is the required formula for the transition rate.

There is another way to derive Fermi's golden rule. Suppose the perturbation does not start at time  $t = 0$  but increases slowly from  $t = -\infty$  by an exponential law  $e^{\eta t}$  with a positive constant  $\eta$  which tends to be zero. Such a process is called *adiabatic switch-on*. In this case the perturbation operator becomes

$$\hat{V}(t) = \hat{V} e^{-i\omega t + \eta t}, \quad (2.53)$$

and  $a_{fi}$  becomes

$$a_{fi} = -\frac{i}{\hbar} \int_{-\infty}^t V_{fi}(\tau) d\tau = -V_{fi} \frac{e^{i(\omega_{fi} - \omega)t + \eta t}}{\hbar(\omega_{fi} - \omega - i\eta)}. \quad (2.54)$$

Hence the squared modulus of  $a_{fi}$  is

$$|a_{fi}|^2 = \frac{1}{\hbar^2} |V_{fi}|^2 \frac{e^{2\eta t}}{(\omega_{fi} - \omega)^2 + \eta^2}. \quad (2.55)$$

The transition rate is given by the time derivative

$$w_{fi} = \frac{d|a_{fi}|^2}{dt} = 2\eta |a_{fi}|^2, \quad (2.56)$$

recalling that  $\lim_{\eta \rightarrow 0} \frac{\eta}{\pi(\alpha^2 + \eta^2)} = \delta(\alpha)$  we obtain the same transition rate formula:

$$w_{fi} = \lim_{\eta \rightarrow 0} \frac{2\pi}{\hbar^2} |V_{fi}|^2 e^{2\eta t} \delta(\omega_{fi} - \omega) = \frac{2\pi}{\hbar} |V_{fi}|^2 \delta(E_f - E_i - \hbar\omega). \quad (2.57)$$

The time dependent perturbation theory can be written in a more compact form using the *interaction picture* formalism. According to (2.40), the formal solution of the wave function  $\Psi(t)$

is

$$\Psi(t) = e^{-\frac{i}{\hbar}\hat{H}t}\Psi(0) = e^{-\frac{i}{\hbar}(\hat{H}_0+\hat{V})t}\Psi(0). \quad (2.58)$$

Now define the wave function in interaction picture  $\phi(t)$  as

$$\phi(t) = e^{\frac{i}{\hbar}\hat{H}_0t}\Psi(t) = e^{\frac{i}{\hbar}\hat{H}_0t}e^{-\frac{i}{\hbar}(\hat{H}_0+\hat{V})t}\Psi(0), \quad (2.59)$$

and the corresponding time evolution equation for  $\phi(t)$  is

$$\begin{aligned} i\hbar\frac{\partial\phi(t)}{\partial t} &= i\hbar\frac{\partial}{\partial t}[e^{\frac{i}{\hbar}\hat{H}_0t}\Psi(t)] \\ &= -e^{\frac{i}{\hbar}\hat{H}_0t}\hat{H}_0\Psi(t) + e^{\frac{i}{\hbar}\hat{H}_0t}(\hat{H}_0 + \hat{V})\Psi(t) \\ &= e^{\frac{i}{\hbar}\hat{H}_0t}\hat{V}e^{-\frac{i}{\hbar}\hat{H}_0t}[e^{\frac{i}{\hbar}\hat{H}_0t}\Psi(t)] \\ &= e^{\frac{i}{\hbar}\hat{H}_0t}\hat{V}e^{-\frac{i}{\hbar}\hat{H}_0t}\phi(t). \end{aligned} \quad (2.60)$$

Now define  $e^{\frac{i}{\hbar}\hat{H}_0t}\hat{V}e^{-\frac{i}{\hbar}\hat{H}_0t}$  as the perturbation operator in interaction picture and denote it by  $\hat{V}_0(t)$ , the equation above can be written as

$$i\hbar\frac{\partial\phi(t)}{\partial t} = \hat{V}_0(t)\phi(t). \quad (2.61)$$

It can be seen that this equation is just the operator form of equation (2.44), thus the time dependent theory is equivalent to interaction picture formalism and the wave function in interaction picture corresponds to the expansion coefficients  $a_k(t)$  in time dependent perturbation theory.

## 2.4 Boltzmann Equation

Boltzmann equation approach is more sophisticated than the Drude theory. It was first derived by Ludwig Boltzmann in 1872 [29–31]. The statistical description of Boltzmann equation is given by the distribution function  $f(\mathbf{r}, \mathbf{k}, t)$ , which is the probability density that an electron with wave vector  $\mathbf{k}$  is at position  $\mathbf{r}$  at time  $t$ . This is a semiclassical description since position  $\mathbf{r}$  and momentum  $\mathbf{p} = \hbar\mathbf{k}$  are determined at the same time. In this section we shall mainly discuss the three dimensional Boltzmann equation. If the interactions are entirely negligible, i.e. a non-interacting system is

considered, then the distribution function obeys Liouville's theorem, according to which we have

$$\frac{df}{dt} = 0. \quad (2.62)$$

In this case the distribution function for electrons is the Fermi-Dirac distribution:

$$f(\mathbf{r}, \mathbf{k}, t) = \frac{1}{e^{(\varepsilon_{\mathbf{k}} - \mu)/T} + 1}, \quad (2.63)$$

and it reduces to the Boltzmann distribution

$$f(\mathbf{r}, \mathbf{k}, t) = e^{(\mu - \varepsilon_{\mathbf{k}})/T} \quad (2.64)$$

when  $\exp[(\varepsilon_{\mathbf{k}} - \mu)/T] \gg 1$ .

In the absence of the external field, all electrons do free motions, and only the coordinates  $\mathbf{r}$  vary. Since the rate of change of  $\mathbf{r}$  is just  $\mathbf{v}$ , we have

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f. \quad (2.65)$$

On the other hand, if there is an external electric field acting on electrons then (recall that the rate of change of a wave vector is  $\hbar \dot{\mathbf{k}} = -e\mathbf{E}$ )

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f - \frac{e}{\hbar} \frac{\partial f}{\partial \mathbf{k}} \cdot \mathbf{E}. \quad (2.66)$$

Equation (2.62) is no longer valid if collisions are taken into account. Instead of (2.62), we must add a collision term  $C(f)$  to the right side of the equation:

$$\frac{df}{dt} = C(f), \quad (2.67)$$

where  $C(f)$  denotes the rate of change of the distribution function due to collisions, and it is called the *collision integral*. Therefore we obtain

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f - \frac{e}{\hbar} \frac{\partial f}{\partial \mathbf{k}} \cdot \mathbf{E} = C(f). \quad (2.68)$$

In principle, once the Boltzmann equation is solved, then the particle current density  $\mathbf{j}$  and electrical current density  $-e\mathbf{j}$  are simply defined as

$$\mathbf{j}(\mathbf{r}, t) = 2 \int \mathbf{v}_{\mathbf{k}} f(\mathbf{r}, \mathbf{k}, t) \frac{d^3 k}{(2\pi)^3}, \quad -e\mathbf{j}(\mathbf{r}, t) = -2e \int \mathbf{v}_{\mathbf{k}} f(\mathbf{r}, \mathbf{k}, t) \frac{d^3 k}{(2\pi)^3}, \quad (2.69)$$

where the factor 2 is due to electron spin degeneracy. And the energy current density  $\mathbf{q}$  and the heat current  $\mathbf{q} - \mu\mathbf{j}$  are

$$\mathbf{q}(\mathbf{r}, t) = 2 \int \varepsilon_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} f(\mathbf{r}, \mathbf{k}, t) \frac{d^3 k}{(2\pi)^3}, \quad (\mathbf{q} - \mu\mathbf{j})(\mathbf{r}, t) = 2 \int (\varepsilon_{\mathbf{k}} - \mu) \mathbf{v}_{\mathbf{k}} f(\mathbf{r}, \mathbf{k}, t) \frac{d^3 k}{(2\pi)^3}. \quad (2.70)$$

The heat current density  $\mathbf{q} - \mu\mathbf{j}$  are evaluated with respect to the chemical potential  $\mu$ , this is the reason why we need to subtract a term  $\mu\mathbf{j}$  from the energy current  $\mathbf{q}$ . If  $\varepsilon_{\mathbf{k}} > \mu$  the particle is said to be “hot” and to carry excess energy, otherwise it is “cold”.

## Transport Relaxation Time

In slightly inhomogeneous cases, the distribution function  $f$  can be written as  $f_0 + \delta f$ , where  $f_0$  is the distribution function in local equilibrium which is a function of energy, while  $\delta f$  is a small correction of  $f_0$ . We write the simplest expression for  $C(f)$  by introducing a phenomenological energy dependent relaxation time  $\tau(\varepsilon)$ :

$$C(f) \approx -\frac{f - f_0}{\tau(\varepsilon)} = -\frac{\delta f}{\tau(\varepsilon)}. \quad (2.71)$$

On the other hand, suppose that the temperature depends on coordinates. Substituting  $f = f_0 + \delta f$  into (2.68) and retaining only the first order term we obtain

$$C(f) = \mathbf{v}_{\mathbf{k}} \cdot \left[ (\varepsilon - \mu) \frac{\nabla T}{T} + e\mathbf{E} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right), \quad (2.72)$$

here we have used

$$\begin{cases} \nabla f_0 = \nabla \left( \frac{1}{e^{(\varepsilon - \mu)/T} + 1} \right) = (\varepsilon - \mu) \frac{\nabla T}{T} \left( -\frac{\partial f_0}{\partial \varepsilon} \right), \\ \frac{\partial f_0}{\partial \mathbf{k}} = \frac{\partial \varepsilon}{\partial \mathbf{k}} \frac{\partial f_0}{\partial \varepsilon} = \hbar \mathbf{v}_{\mathbf{k}} \left( \frac{\partial f_0}{\partial \varepsilon} \right). \end{cases} \quad (2.73)$$

Therefore a connection between the correction to the distribution function  $\delta f$ , the transport relaxation time  $\tau$  and the collision integral  $C(f)$  is reached:

$$\delta f = -\tau C(f) = -\tau(\varepsilon_{\mathbf{k}})\mathbf{v}_{\mathbf{k}} \cdot \left[ (\varepsilon_{\mathbf{k}} - \mu)\frac{\nabla T}{T} + e\mathbf{E} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right). \quad (2.74)$$

The collision integral can also be determined by Fermi's golden rule. Consider the case that electrons are scattered by random impurities with short range elastic scattering. Let the density of impurities be denoted by  $n_{\text{imp}}$ . Because electrons are fermions, the probability density of an electron transiting from  $\mathbf{k}'$  state to  $\mathbf{k}$  is

$$\frac{2\pi}{\hbar}n_{\text{imp}}|T_{\mathbf{k}\mathbf{k}'}|^2\delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})f(\mathbf{r}, \mathbf{k}', t)[1 - f(\mathbf{r}, \mathbf{k}, t)], \quad (2.75)$$

where  $T_{\mathbf{k}\mathbf{k}'}$  is the scattering  $T$ -matrix. Similarly, the probability density of transition from  $\mathbf{k}$  state to  $\mathbf{k}'$  state is

$$\frac{2\pi}{\hbar}n_{\text{imp}}|T_{\mathbf{k}\mathbf{k}'}|^2\delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})f(\mathbf{r}, \mathbf{k}, t)[1 - f(\mathbf{r}, \mathbf{k}', t)]. \quad (2.76)$$

Therefore the collision integral can be written as

$$\begin{aligned} C(f) &= \frac{2\pi}{\hbar}n_{\text{imp}} \int \frac{d^3\mathbf{k}'}{(2\pi)^3} |T_{\mathbf{k}\mathbf{k}'}|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) \{f(\mathbf{r}, \mathbf{k}', t)[1 - f(\mathbf{r}, \mathbf{k}, t)] - f(\mathbf{r}, \mathbf{k}, t)[1 - f(\mathbf{r}, \mathbf{k}', t)]\} \\ &= \frac{2\pi}{\hbar}n_{\text{imp}} \int \frac{d^3\mathbf{k}'}{(2\pi)^3} |T_{\mathbf{k}\mathbf{k}'}|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) [f(\mathbf{r}, \mathbf{k}', t) - f(\mathbf{r}, \mathbf{k}, t)] \\ &= \frac{2\pi}{\hbar}n_{\text{imp}} \int \frac{d^3\mathbf{k}'}{(2\pi)^3} |T_{\mathbf{k}\mathbf{k}'}|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) [\delta f(\mathbf{r}, \mathbf{k}', t) - \delta f(\mathbf{r}, \mathbf{k}, t)]. \end{aligned} \quad (2.77)$$

In such approximations an isotropic dispersion relation  $\varepsilon(\mathbf{k})$  is usually adopted, to be specific,  $\varepsilon(\mathbf{k}) = \hbar^2\mathbf{k}^2/2m^*$ . This dispersion relation has the same form as the dispersion relation of free particles but with an effective mass. Hence the delta function in the above expression forces both  $\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}'}$  and  $|\mathbf{k}| = |\mathbf{k}'|$ , and the two velocities  $\mathbf{v}_{\mathbf{k}}$  and  $\mathbf{v}_{\mathbf{k}'}$  differ only in their direction. It can be seen from (2.74) that  $\delta f$  can be written in a form  $\mathbf{v} \cdot \mathbf{A}$ , where  $\mathbf{A}$  is a vector consisting of all other terms besides  $\mathbf{v}$  in (2.74). Now denote the angle between  $\mathbf{k}$  and  $\mathbf{A}$  by  $\theta$ , similarly denote the angle between  $\mathbf{k}'$  and  $\mathbf{A}$  by  $\theta'$ , hence

$$\delta f(\mathbf{k}') - \delta f(\mathbf{k}) = \mathbf{v}_{\mathbf{k}'} \cdot \mathbf{A} - \mathbf{v}_{\mathbf{k}} \cdot \mathbf{A} = vA(\cos \theta' - \cos \theta), \quad (2.78)$$

where  $v = |\mathbf{v}|$  and  $A = |\mathbf{A}|$ . Since the  $T$ -matrix  $T_{\mathbf{k}\mathbf{k}'}$  depends only on the angle between  $\mathbf{k}$  and  $\mathbf{k}'$ , we now denote this angle by  $\alpha$  and try to express the above formula with  $\alpha$ . Take the direction of  $\mathbf{k}$  as the polar axis and build a spherical coordinate system. Let  $\varphi$  and  $\varphi'$  be the azimuth angles of  $\mathbf{A}$  and  $\mathbf{k}'$  in this spherical system, then

$$\cos \theta' = \cos \theta \cos \alpha + \sin \theta \sin \alpha \cos(\varphi - \varphi'). \quad (2.79)$$

The azimuth angles  $\varphi$  and  $\varphi'$  do not appear else where in the integrand of (2.77), so when integrating over  $d\varphi'$ , the term in  $\cos(\varphi - \varphi')$  averages to zero. Therefore in (2.77) we can just omit the term in  $\cos(\varphi - \varphi')$  and write

$$\begin{aligned} C(f) &= -\frac{2\pi}{\hbar} n_{\text{imp}} \int \frac{d^3\mathbf{k}'}{(2\pi)^3} |T_{\mathbf{k}\mathbf{k}'}|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) v A \cos \theta (1 - \cos \alpha) \\ &= -\frac{2\pi}{\hbar} n_{\text{imp}} \int \frac{d^3\mathbf{k}'}{(2\pi)^3} |T_{\mathbf{k}\mathbf{k}'}|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) \mathbf{v} \cdot \mathbf{A} (1 - \cos \alpha) \\ &= -\frac{2\pi}{\hbar} n_{\text{imp}} \int \frac{d^3\mathbf{k}'}{(2\pi)^3} |T_{\mathbf{k}\mathbf{k}'}|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) (1 - \cos \alpha) \delta f(\mathbf{r}, \mathbf{k}, t). \end{aligned} \quad (2.80)$$

Because the collision integral  $C(f) = -\delta f/\tau$ , comparing with the above formula we obtain an expression for the transport relaxation time

$$\frac{1}{\tau(\varepsilon)} = \frac{2\pi}{\hbar} n_{\text{imp}} \int \frac{d^3\mathbf{k}'}{(2\pi)^3} |T_{\mathbf{k}\mathbf{k}'}|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'}) (1 - \cos \alpha). \quad (2.81)$$

The extra factor  $1 - \cos \alpha$  measures how much an electron scatters: larger scattering angle  $\alpha$  makes this factor larger and contributes more to the resistivity and decreases the conductivity.

Now let us return to (2.68) and substitute  $f = f_0 + \delta f$ . Because  $f_0$  does not depend on time we write  $\frac{\partial f}{\partial t} = \frac{\partial \delta f}{\partial t}$ , and write  $\nabla f = \nabla f_0$ ,  $\frac{\partial f}{\partial \mathbf{k}} = \frac{\partial f_0}{\partial \mathbf{k}}$  since  $\delta f$  is small compared to  $f_0$ . Substituting  $C(f) = -\delta f/\tau$  we can finally write a linearized Boltzmann equation as

$$\frac{\partial \delta f}{\partial t} + \mathbf{v}_{\mathbf{k}} \cdot \left[ (\varepsilon - \mu) \frac{\nabla T}{T} + e \mathbf{E} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right) = -\frac{\delta f}{\tau}. \quad (2.82)$$

Writing the second term of the left side of the above equation as  $\mathbf{v}_{\mathbf{k}} \cdot \mathbf{F}$  the equation becomes

$$\frac{\partial \delta f}{\partial t} + \mathbf{v}_{\mathbf{k}} \cdot \mathbf{F} = -\frac{\delta f}{\tau}, \quad (2.83)$$

and it can be seen that  $\mathbf{F}$  acts as the driving term. Applying a Fourier transform on both sides of the equation we shall get

$$\delta f_\omega = \frac{\tau \mathbf{v} \cdot \mathbf{F}_\omega}{1 - i\omega\tau}, \quad (2.84)$$

this is a Drude like formula. It shows that Drude formula can be derived from Boltzmann's equation and puts the Drude theory on a much firmer theoretical basis.

### Transport Coefficients

Because in equilibrium there is no net current, the integrals in current formulas (2.69) and (2.70) are zero when  $f = f_0$ . Therefore formulas for the electricity and heat currents may be written as

$$-e\mathbf{j} = -2e \int \mathbf{v} \delta f \frac{d^3k}{(2\pi)^3}, \quad \mathbf{q} - \mu\mathbf{j} = 2 \int (\varepsilon - \mu) \mathbf{v} \delta f \frac{d^3k}{(2\pi)^3}. \quad (2.85)$$

Substituting (2.74) into the above formulas gives

$$-e\mathbf{j} = 2e \int \tau(\varepsilon_{\mathbf{k}}) \mathbf{v}_{\mathbf{k}} \cdot \left[ (\varepsilon_{\mathbf{k}} - \mu) \frac{\mathbf{v}_{\mathbf{k}} \cdot \nabla T}{T} + e \mathbf{v}_{\mathbf{k}} \cdot \mathbf{E} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3k}{(2\pi)^3}, \quad (2.86)$$

$$\mathbf{q} - \mu\mathbf{j} = -2 \int \tau(\varepsilon_{\mathbf{k}}) (\varepsilon_{\mathbf{k}} - \mu) \mathbf{v}_{\mathbf{k}} \cdot \left[ (\varepsilon_{\mathbf{k}} - \mu) \frac{\mathbf{v}_{\mathbf{k}} \cdot \nabla T}{T} + e \mathbf{v}_{\mathbf{k}} \cdot \mathbf{E} \right] \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3k}{(2\pi)^3}. \quad (2.87)$$

These currents can be viewed as responses to the electric field and the temperature gradient:

$$-e\mathbf{j} = \sigma[\mathbf{E} - S\nabla T], \quad \mathbf{q} - \mu\mathbf{j} = \sigma ST\mathbf{E} - k\nabla T, \quad (2.88)$$

where  $\sigma$  is the electrical conductivity,  $S$  is the *Seebeck coefficient*, and  $k$  is the thermal conductivity due to the electrons. Let  $\theta$  be the angle between  $\mathbf{v}_{\mathbf{k}}$  and the electric field  $\mathbf{E}$ , then when there is no temperature gradient the electricity current is

$$\begin{aligned} -e\mathbf{j} &= 2e^2 \int \tau(\varepsilon_{\mathbf{k}}) \mathbf{v}_{\mathbf{k}} \cdot (\mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}) \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3k}{(2\pi)^3} \\ &= 2e^2 \int \tau(\varepsilon_{\mathbf{k}}) \mathbf{v}_{\mathbf{k}} (v_{\mathbf{k}} E \cos \theta) \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3k}{(2\pi)^3}. \end{aligned} \quad (2.89)$$

In a lattice with cubic symmetry, the currents are in the same direction of the driving term<sup>2</sup>, so for the term  $\mathbf{v}_{\mathbf{k}}$  in the integral only the component with the same direction of  $\mathbf{E}$  remains, which means we can rewrite  $\mathbf{v}_{\mathbf{k}}$  as  $v_{\mathbf{k}} \frac{\mathbf{E}}{E} \cos \theta$  in the integral. Hence

$$-e\mathbf{j} = 2e^2 \int \tau(\varepsilon_{\mathbf{k}}) v_{\mathbf{k}}^2 \cos^2 \theta \mathbf{E} \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}. \quad (2.90)$$

Since the solid angle integral  $\int \cos^2 \theta \sin \theta d\theta d\phi = \frac{1}{3}$ , we finally reach a formula for the electrical conductivity

$$\sigma = \frac{2e^2}{3} \int \tau(\varepsilon_{\mathbf{k}}) v_{\mathbf{k}}^2 \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}. \quad (2.91)$$

Similarly, the formulas for other transport coefficients due to electrons are

$$\sigma S = -\frac{2e}{3T} \int \tau(\varepsilon_{\mathbf{k}}) (\varepsilon_{\mathbf{k}} - \mu) v_{\mathbf{k}}^2 \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}, \quad (2.92)$$

$$k = \frac{2}{3T} \int \tau(\varepsilon_{\mathbf{k}}) (\varepsilon_{\mathbf{k}} - \mu)^2 v_{\mathbf{k}}^2 \left( -\frac{\partial f_0}{\partial \varepsilon} \right) \frac{d^3 k}{(2\pi)^3}. \quad (2.93)$$

The physical meaning of the electrical conductivity  $\sigma$  is the response coefficient to the external electric field, and the thermal conductivity  $k$  is the response coefficient to the temperature gradient, but the physical meaning of the Seebeck coefficient  $S$  is not so clear. The electricity current is given by (2.88). Consider a situation where there is no electricity current. Then

$$\sigma \mathbf{E} = S \nabla T, \quad (2.94)$$

multiplying both sides by a spatial vector  $\mathbf{l}$  which has same direction with  $\mathbf{E}$  we obtain

$$\sigma \mathbf{E} \cdot \mathbf{l} = S (\nabla T \cdot \mathbf{l}). \quad (2.95)$$

Since  $\mathbf{E} \cdot \mathbf{l}$  is just the voltage difference  $-\Delta V$  and  $\nabla T \cdot \mathbf{l}$  is the temperature difference  $\Delta T$ , the Seebeck coefficient can be written as

$$S = -\frac{\Delta V}{\Delta T}. \quad (2.96)$$

---

<sup>2</sup>In principle all these transport coefficients are tensors  $\sigma_{\alpha\beta}$ ,  $S_{\alpha\beta}$  and  $k_{\alpha\beta}$ , here  $\alpha, \beta$  is the spatial component  $x, y, z$ .



It can be seen that the temperature difference induces a voltage difference, this phenomenon is called the *Seebeck effect*.

Equation (2.88) can also be rearranged as the heat current equation

$$\sigma \mathbf{E} = -e\mathbf{j} + \sigma S \nabla T, \quad \mathbf{q} - \mu \mathbf{j} = -e\mathbf{j} S T - (k - \sigma T S^2) \nabla T. \quad (2.97)$$

The thermal conductivity  $k$  is measured with no electric field, while the quantity  $k - \sigma T S^2$  is measured with no electricity current. Note that the thermal conductivity  $k$  discussed here includes all other thermal effects besides the effect of electrons, such as the phonon effects, and is not only due to electrons. It can be seen that there can be heat current even when  $-e\mathbf{j}$  is zero, thus the quantity  $k - \sigma T S^2$  is the thermal conductivity with electrons excluded. Now define a quantity  $Z$  as

$$Z = \frac{\sigma S^2}{k - \sigma T S^2} \quad \text{and} \quad ZT = \frac{\sigma T S^2}{k - \sigma T S^2}, \quad (2.98)$$

which is called the *figure of merit* for thermoelectric materials. Equation (2.97) also shows that a heat current can be driven by electricity current. This phenomenon is the basis of thermoelectric refrigerators where the heat is driven from the cold to the hot part by an electricity current. The difference between  $k$  and  $k - \sigma T S^2$  is larger with larger  $ZT$ . In particular,  $(k - \sigma T S^2) \rightarrow 0$  when  $ZT \rightarrow \infty$ , in this case all heat is carried by electrons and the refrigerator reaches the theoretical best performance.

## 2.5 The Generalized Susceptibility

In the previous sections some response coefficients have been discussed like electricity conductivity. This type of coefficients describe the behavior of the system under an external perturbation. In this section we shall discuss the general properties of such kind of coefficients. This is also the starting point for linear response theory.

An external perturbation is described, in the Hamiltonian, by a perturbing operator of the type

$$\hat{V}(t) = -\hat{x}f(t), \quad (2.99)$$

where  $\hat{x}$  is the operator of the physical quantity concerned, and  $f(t)$  is the *generalized force* which represents the external field. Assume that the quantum mean value  $\bar{x}$  is zero in the equilibrium state when in the absence of the perturbation. Then  $\bar{x}$  is not zero when a perturbation is present. It is clear that the value of  $\bar{x}$  can only depend on the values of  $f(t)$  at previous times, i.e. the history of  $f(t)$ , and this is called the *causality principle*. Therefore  $\bar{x}(t)$  can be written in the form

$$\bar{x}(t) = \int_0^{\infty} \alpha(\tau) f(t - \tau) d\tau, \quad (2.100)$$

where  $\alpha(\tau)$  is a real function of time. Note that  $\alpha(\tau)$  is defined to be zero when  $\tau < 0$  due to the causality principle. In this sense  $\alpha(\tau)$  is a retarded quantity like the retarded Green's function<sup>3</sup>. The quantity  $\bar{x}(t)$  is called the *response* of the system to the perturbation, and  $\alpha(\tau)$  is called the *generalized susceptibility* [32, 33].

Applying a Fourier transform to (2.100) we obtain the relationship between the Fourier components of the force  $f_\omega$ , the susceptibility  $\alpha(\omega)$  and the response  $\bar{x}_\omega$  as

$$\bar{x}_\omega = \alpha(\omega) f_\omega, \quad (2.101)$$

where

$$\alpha(\omega) = \int_0^{\infty} \alpha(t) e^{i\omega t} dt, \quad (2.102)$$

and

$$\bar{x}_\omega = \int_{-\infty}^{\infty} \bar{x}(t) e^{i\omega t} dt, \quad f_\omega = \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt. \quad (2.103)$$

Once the generalized susceptibility  $\alpha(\omega)$  is specified, the behavior of the system under the perturbation is completely determined, thus it plays a fundamental role in the response theory. The function  $\alpha(\omega)$  is usually complex, denote its real and imaginary parts by  $\alpha'$  and  $\alpha''$ :

$$\alpha(\omega) = \alpha'(\omega) + i\alpha''(\omega). \quad (2.104)$$

The definition (2.102) shows that

$$\alpha(-\omega) = \alpha^*(\omega). \quad (2.105)$$

---

<sup>3</sup>In fact, in linear response region it is just the negative of the retarded Green's function.

Separating the real and imaginary parts, we find that

$$\alpha'(-\omega) = \alpha'(\omega), \quad \alpha''(-\omega) = -\alpha''(\omega), \quad (2.106)$$

which means that  $\alpha'(\omega)$  is an even function of  $\omega$  and  $\alpha''(\omega)$  is an odd function of  $\omega$ . This property is simply the consequence of the fact that the response  $\bar{x}$  must be real for any real force  $f$ . And we shall suppose  $\alpha(\omega) \rightarrow 0$  when  $\omega \rightarrow \pm\infty$ , since  $\alpha(t)$  should tend to zero<sup>4</sup> when  $t \rightarrow \infty$ , and due to the fast oscillation factor  $\lim_{\omega \rightarrow \pm\infty} e^{\pm i\omega t}$  the integral in (2.102) would average to zero.

It is possible to derive some very general properties of  $\alpha(\omega)$  by just using the theory of functions of a complex variable. Now we regard  $\omega$  as a complex variable, i.e.,  $\omega = \omega' + i\omega''$ . From the definition (2.102) it immediately shows that  $\alpha(\omega)$  is a regular function everywhere in the upper half-plane. For when  $\omega'' > 0$  there is an exponentially decreasing factor  $e^{-\omega''t}$  in the integrand in (2.102), and since  $\alpha(t)$  is finite for all positive  $t$ , the integral converges. On other hand, in the lower half-plane, the decreasing factor in (2.102) becomes an increasing factor, so the integral diverges. Hence the function  $\alpha(\omega)$  in the lower half-plane can only be defined as the analytic continuation of  $\alpha(\omega)$  in upper half-plane. It is worth noticing that the conclusion  $\alpha(\omega)$  is regular in the upper half-plane is physically a consequence of the causality principle. And equation (2.105) can be generalized from the real axis into the upper half-plane as

$$\alpha(-\omega^*) = \alpha^*(\omega). \quad (2.107)$$

Let us now derive an important relationship between the real and imaginary parts of  $\alpha(\omega)$ . To do so, we choose a positive  $\omega_0$  in real axis and integrate the expression  $\alpha(\omega)/(\omega - \omega_0)$  around the contour  $C$  shown in Figure 2.1. This contour is indented upwards at the point  $\omega = \omega_0$  and includes the whole real axis, and is finally completed by an infinite semicircle. Since  $\alpha(\omega)$  is regular in the upper half-plane and the point  $\omega = \omega_0$  has been excluded from the integration region, the function  $\alpha(\omega)/(\omega - \omega_0)$  is everywhere analytic inside the contour  $C$ , then according to the residue theorem we have

$$\int_C \frac{\alpha(\omega)}{\omega - \omega_0} d\omega = 0. \quad (2.108)$$

---

<sup>4</sup>It just means that the history very long ago has little direct effect in the present.

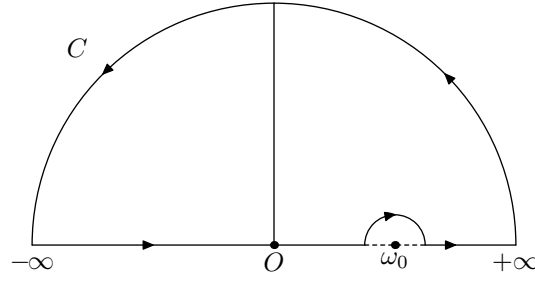


Figure 2.1: Integration contour for  $\frac{\alpha(\omega)}{\omega - \omega_0}$ .

The function  $\alpha(\omega)/(\omega - \omega_0)$  tends to zero more rapidly than  $1/\omega$  since  $\alpha(\omega) \rightarrow 0$  at infinite, therefore the integral along the infinite semicircle is also zero. The point  $\omega_0$  is avoided by an infinitesimal semicircle, we now denote the radius of this semicircle by  $r$  which tends to zero. According to residue theorem, the integral along an infinitesimal full circle around  $\omega_0$  is  $-2i\pi\alpha(\omega_0)$ , therefore the integral along the infinitesimal semicircle is just  $-i\pi\alpha(\omega_0)$ . The integration along the whole real axis therefore gives

$$\lim_{r \rightarrow 0} \left[ \int_{-\infty}^{\omega_0 - r} \frac{\alpha(\omega)}{\omega - \omega_0} + \int_{\omega_0 + r}^{\infty} \frac{\alpha(\omega)}{\omega - \omega_0} \right] - i\pi\alpha(\omega_0) = 0. \quad (2.109)$$

The first term is just the *Cauchy principal value* of the integral from  $-\infty$  to  $\infty$ . Writing the formula in the usual Cauchy principal value notation, we have

$$i\pi\alpha(\omega_0) = P \int_{-\infty}^{\infty} \frac{\alpha(\omega)}{\omega - \omega_0} d\omega. \quad (2.110)$$

We now replace the integration variable  $\omega$  by  $\xi$  which takes only real values, and replace the given real value  $\omega_0$  by  $\omega$ . Separating the real and imaginary parts of (2.110), the following formulas for real  $\omega$  are obtained:

$$\alpha'(\omega) = -\frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\alpha''(\xi)}{\omega - \xi} d\xi, \quad (2.111)$$

$$\alpha''(\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{\alpha'(\xi)}{\omega - \xi} d\xi. \quad (2.112)$$

The above formulas are called *dispersion relations*, or more commonly *Kramers-Kronig relations*, and were first derived by Hans Kramers [34] and Ralph Kronig [35]. It should be emphasized that

the proof is essentially based only on the property of  $\alpha(\omega)$  that it is regular in the upper plane. Thus the Kramers-Kronig relations are also a direct consequence of the causality principle.

## 2.6 The Fluctuation-Dissipation Theorem

The generalized susceptibility is directly related to the dissipation processes of the system. In this section we shall derive the formula which represents such a relationship.

If the generalized force  $f$  is purely monochromatic and given by

$$f(t) = \text{Re } f_0 e^{-i\omega t} = \frac{1}{2}(f_0 e^{-i\omega t} + f_0^* e^{i\omega t}), \quad (2.113)$$

then according to (2.101) we obtain

$$\bar{x}(t) = \frac{1}{2}[\alpha(\omega)f_0 e^{-i\omega t} + \alpha(-\omega)f_0^* e^{i\omega t}]. \quad (2.114)$$

When the generalized force  $f$  acts on the system, the system would absorb energy from the external source, which can be converted into heat. This process is called *dissipation*. Recall that the energy change of the system is expressed by the equation  $dE/dt = \langle \partial \hat{H} / \partial t \rangle$  [32], which states that the time derivative of the mean energy is equal to the mean value of the partial derivative of the Hamiltonian. Because only the generalized force  $f(t)$  depends explicitly on time in the Hamiltonian, we have

$$\frac{dE}{dt} = -\bar{x} \frac{df(t)}{dt}. \quad (2.115)$$

Substitute (2.113) and (2.114) into the above expression, then

$$\begin{aligned} \frac{dE}{dt} &= \frac{1}{4}[\alpha(\omega)f_0 e^{-i\omega t} + \alpha(-\omega)f_0^* e^{i\omega t}](-i\omega f_0 e^{-i\omega t} + i\omega f_0^* e^{i\omega t}) \\ &= \frac{1}{4}[-i\omega\alpha(\omega)f_0^2 e^{-2i\omega t} + i\omega\alpha(\omega)|f_0|^2 - i\omega\alpha(-\omega)|f_0|^2 + i\omega\alpha(-\omega)(f_0^*)^2 e^{2i\omega t}], \end{aligned} \quad (2.116)$$

the terms containing  $e^{\pm 2i\omega t}$  factors would vanish when averaging with time, therefore on averaging

with time we obtain

$$\begin{aligned}
\frac{dE}{dt} &= \frac{1}{4}i\omega[\alpha(\omega) - \alpha(-\omega)]|f_0|^2 \\
&= \frac{1}{4}i\omega[\alpha(\omega) - \alpha^*(\omega)]|f_0|^2 \\
&= \frac{1}{2}\omega\alpha''(\omega)|f_0|^2.
\end{aligned} \tag{2.117}$$

From this formula we see that the dissipation energy can be expressed in terms of the imaginary part of the generalized susceptibility.

Using Fermi's golden rule we can also derive an explicit formula for  $dE/dt$ . Under the perturbation

$$\hat{V}(t) = -f(t)\hat{x} = -\frac{1}{2}(f_0e^{-i\omega t} + f_0^*e^{i\omega t})\hat{x} \tag{2.118}$$

the system make transitions, and the transition rate from state  $n$  to state  $m$  (here suppose states  $n$  and  $m$  are eigenstates of the unperturbed system with eigenenergy  $E_n$  and  $E_m$ , and  $\omega_{mn} = (E_m - E_n)/\hbar$ ) is given by

$$w_{mn} = \frac{\pi|f_0|^2}{2\hbar^2}|x_{mn}|^2[\delta(\omega + \omega_{mn}) + \delta(\omega + \omega_{nm})], \tag{2.119}$$

where  $x_{mn}$  stands for  $\langle m|\hat{x}|n\rangle$  and we have used the fact that  $x_{mn} = x_{nm}^*$ . In each transition the system absorbs or emits an energy  $\hbar\omega_{mn}$ . Suppose the system is in a canonical distribution with the distribution function  $\rho_n = e^{(F-E_n)/T}$ , where  $F$  is the free energy of the system. Define the energy change per unit time by  $Q$ , then

$$\begin{aligned}
Q &= \frac{dE}{dt} = \sum_{nm} \rho_n w_{mn} \hbar\omega_{mn} \\
&= \frac{\pi}{2\hbar}|f_0|^2 \sum_{mn} \rho_n |x_{mn}|^2 [\delta(\omega + \omega_{mn}) + \delta(\omega + \omega_{nm})] \omega_{mn},
\end{aligned} \tag{2.120}$$

or, because the delta functions force  $\omega_{mn} = \pm\omega$ ,

$$Q = \frac{\pi}{2\hbar}\omega|f_0|^2 \sum_{mn} \rho_n |x_{mn}|^2 [\delta(\omega + \omega_{nm}) - \delta(\omega + \omega_{mn})]. \tag{2.121}$$

Comparison between this formula and (2.117) gives

$$\alpha''(\omega) = \frac{\pi}{\hbar} \sum_{mn} \rho_n |x_{mn}|^2 [\delta(\omega + \omega_{nm}) - \delta(\omega + \omega_{mn})]. \quad (2.122)$$

There is also a relationship between the fluctuations of the physical quantity  $x$  and the imaginary part of  $\alpha$ . To show this, we first define the quantum correlation function for  $\hat{x}$  as

$$\phi(t) = \frac{1}{2} \langle \hat{x}(t)\hat{x}(0) + \hat{x}(0)\hat{x}(t) \rangle, \quad (2.123)$$

and its Fourier transform as

$$\phi(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} \langle \hat{x}(t)\hat{x}(0) + \hat{x}(0)\hat{x}(t) \rangle e^{i\omega t} dt. \quad (2.124)$$

If the system is in canonical distribution, we can write  $\phi(t)$  as

$$\begin{aligned} \phi(t) &= \frac{1}{2} \sum_{nm} \rho_n [x_{nm}(t)x_{mn} + x_{nm}x_{mn}(t)] \\ &= \frac{1}{2} \sum_{nm} \rho_n |x_{mn}|^2 (e^{i\omega_{nm}t} + e^{i\omega_{mn}t}). \end{aligned} \quad (2.125)$$

Recall that for delta function

$$\delta(a) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ipa} dp = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ipa} dp, \quad (2.126)$$

then we obtain

$$\begin{aligned} \phi(\omega) &= \frac{1}{2} \sum_{nm} \int_{-\infty}^{\infty} \rho_n |x_{mn}|^2 [e^{i(\omega+\omega_{nm})t} + e^{i(\omega+\omega_{mn})t}] dt \\ &= \pi \sum_{nm} \rho_n |x_{mn}|^2 [\delta(\omega + \omega_{nm}) + \delta(\omega + \omega_{mn})]. \end{aligned} \quad (2.127)$$

Since the summation now is over both suffixes  $m$  and  $n$ , they can be interchanged. Hence we can write

$$\begin{aligned} \phi(\omega) &= \pi \sum_{nm} (\rho_n + \rho_m) |x_{mn}|^2 \delta(\omega + \omega_{nm}) \\ &= \pi \sum_{nm} \rho_n (1 + e^{\hbar\omega_{nm}/T}) |x_{mn}|^2 \delta(\omega + \omega_{nm}), \end{aligned} \quad (2.128)$$

or, due to the delta function in the summation  $\omega_{nm}$  can be replaced by  $-\omega$ ,

$$\phi(\omega) = \pi(1 + e^{-\hbar\omega/T}) \sum_{nm} \rho_n |x_{mn}|^2 \delta(\omega + \omega_{nm}). \quad (2.129)$$

Similarly we can also write  $\alpha''(\omega)$  as

$$\alpha''(\omega) = \frac{\pi}{\hbar}(1 - e^{-\hbar\omega/T}) \sum_{nm} \rho_n |x_{mn}|^2 \delta(\omega + \omega_{nm}). \quad (2.130)$$

A comparison between the above two expressions gives

$$\phi(\omega) = \hbar\alpha''(\omega) \coth \frac{\hbar\omega}{2T}. \quad (2.131)$$

The fluctuation properties of  $x$  are characterized by the mean square  $\langle \hat{x}^2 \rangle$  which is just  $\phi(t=0)$ , hence

$$\langle \hat{x}^2 \rangle = \hbar \lim_{t \rightarrow 0} \int_{-\infty}^{\infty} \alpha''(\omega) \coth \frac{\hbar\omega}{2T} e^{-i\omega t} \frac{d\omega}{2\pi} = \frac{\hbar}{\pi} \int_0^{\infty} \alpha''(\omega) \coth \frac{\hbar\omega}{2T} d\omega. \quad (2.132)$$

These formulas constitute an important theorem which is called the *fluctuation-dissipation theorem*, originally formulated by Harry Nyquist in 1928 [36] and then proved by Herbert Callen and Theodore Welton in 1951 [37]. This theorem establishes a relationship between the fluctuation and dissipative properties of the system.

When temperature is high that  $T \gg \hbar\omega$  we have  $\coth(\hbar\omega/2T) \approx 2T/\hbar\omega$ , and the formula (2.131) becomes

$$\phi(\omega) = \frac{2T}{\omega} \alpha''(\omega), \quad (2.133)$$

the Plank constant  $\hbar$  disappears in the formula, because under such a condition the fluctuations are considered to be classical. In this case (2.132) then becomes

$$\langle \hat{x}^2 \rangle = \frac{2T}{\pi} \int_0^{\infty} \frac{\alpha''(\omega)}{\omega} d\omega = -\frac{2T}{\pi} \int_0^{\infty} \frac{\alpha''(\omega)}{0-\omega} d\omega, \quad (2.134)$$

using the Kramers-Kronig relation (note that  $\alpha'(0) = \alpha(0)$ ) the mean square of fluctuations can be



expressed by the static value  $\alpha(\omega = 0)$ :

$$\langle \hat{x}^2 \rangle = T\alpha(0). \quad (2.135)$$

### The Fluctuation-Dissipation Theorem for Multiple Variables

The fluctuation-dissipation theorem can be generalized to multiple variables. Denote the physical quantities by  $x_i$ , and the operator of the perturbation then becomes

$$\hat{V}(t) = - \sum_i \hat{x}_i f_i(t), \quad (2.136)$$

and the generalized susceptibility is defined as a tensor  $\alpha_{ik}(\tau)$ :

$$\bar{x}_i = \sum_k \int_0^\infty \alpha_{ik}(\tau) f_k(t - \tau) d\tau. \quad (2.137)$$

Writing the above formula in Fourier component form we get

$$\bar{x}_{i\omega} = \sum_k \alpha_{ik}(\omega) f_{k\omega}. \quad (2.138)$$

Now consider the case where the generalized forces are purely monochromatic with frequency  $\omega$ , then  $f_i$  can be written as

$$f_i(t) = \frac{1}{2} (f_{0i} e^{-i\omega t} + f_{0i}^* e^{i\omega t}), \quad (2.139)$$

and the corresponding responses  $\bar{x}_i$  are

$$\bar{x}_i(t) = \frac{1}{2} \sum_k [\alpha_{ik}(\omega) f_{0k} e^{-i\omega t} + \alpha_{ik}^*(\omega) f_{0k}^* e^{i\omega t}]. \quad (2.140)$$

The energy change per unit time of the system is (note that after averaging over time the terms in oscillation factor  $e^{\pm 2i\omega t}$  vanish)

$$\begin{aligned}
Q &= -\sum_i \bar{x}_i(t) \dot{f}_i(t) \\
&= -i\omega \sum_{ik} [\alpha_{ik}(\omega) f_{0k} f_{0i}^* - \alpha_{ik}^*(\omega) f_{0k}^* f_{0i}] \\
&= i\omega \sum_{ik} [\alpha_{ik}^*(\omega) - \alpha_{ik}(\omega)] f_{0i} f_{0k}^*,
\end{aligned} \tag{2.141}$$

where in the last step the suffixes  $i$  and  $k$  of the first term in the summation are interchanged.

On the other hand, the energy change per unit time is given by Fermi's golden rule as

$$\begin{aligned}
Q &= \frac{\pi}{2\hbar} \sum_{ik,mn} \rho_n(x_i)_{mn}(x_k)_{nm} [f_{0i} f_{0k}^* \delta(\omega + \omega_{nm}) + f_{0i}^* f_{0k} \delta(\omega + \omega_{mn})] \omega_{mn} \\
&= \frac{\pi}{2\hbar} \omega \sum_{ik,mn} \rho_n(x_i)_{mn}(x_k)_{nm} [f_{0i} f_{0k}^* \delta(\omega + \omega_{nm}) - f_{0i}^* f_{0k} \delta(\omega + \omega_{mn})] \\
&= \frac{\pi}{2\hbar} \omega \sum_{ik,mn} \rho_n f_{0i} f_{0k}^* [(x_i)_{mn}(x_k)_{nm} \delta(\omega + \omega_{nm}) - (x_i)_{nm}(x_k)_{mn} \delta(\omega + \omega_{mn})],
\end{aligned} \tag{2.142}$$

comparing with (2.141) we find that

$$\alpha_{ik}^* - \alpha_{ki} = -\frac{2\pi i}{\hbar} \sum_{mn} \rho_n [(x_i)_{mn}(x_k)_{nm} \delta(\omega + \omega_{nm}) - (x_i)_{nm}(x_k)_{mn} \delta(\omega + \omega_{mn})]. \tag{2.143}$$

Now define the correlation function for  $x_i$  as

$$\phi_{ik}(t) = \frac{1}{2} \langle \hat{x}_i(t) \hat{x}_k(0) + \hat{x}_k(0) \hat{x}_i(t) \rangle, \tag{2.144}$$

its Fourier components are accordingly

$$\phi_{ik}(\omega) = \pi \sum_{nm} \rho_n [(x_i)_{nm}(x_k)_{mn} \delta(\omega + \omega_{nm}) + (x_k)_{nm}(x_i)_{mn} \delta(\omega + \omega_{mn})]. \tag{2.145}$$

A comparison with (2.143) gives

$$\phi_{ik}(\omega) = \frac{i}{2} \hbar (\alpha_{ki}^* - \alpha_{ik}) \coth \frac{\hbar\omega}{2T}, \tag{2.146}$$

and thus we obtain the fluctuation-dissipation theorem for multiple variables.

Similar to (2.135), the mean square of fluctuations can be expressed by the static susceptibility  $\alpha_{ik}(\omega = 0)$ :

$$\frac{1}{2}\langle\hat{x}_i\hat{x}_k + \hat{x}_k\hat{x}_i\rangle = T\alpha_{ik}(0). \quad (2.147)$$

## 2.7 The Kubo-Greenwood Formula

The Drude formula and Boltzmann equation methods are classical or semiclassical. Now we proceed to obtain a quantum mechanical expression for electricity conductivity based on the *independent-particle approximation*. It is also the simplest practical formula in linear response theory.

The electromagnetic interaction in classical electrodynamics is described by the term<sup>5</sup>  $e\mathbf{j} \cdot \mathbf{A}$ , where  $\mathbf{j}$  is the electron particle current density and  $\mathbf{A}$  is the vector potential of the electromagnetic four-potential. In quantum electrodynamics  $\mathbf{j}$  and  $\mathbf{A}$  should both be replaced by corresponding operators  $\hat{\mathbf{j}}$  and  $\hat{\mathbf{A}}$ . However, here we need only to replace  $\mathbf{j}$  by its operator  $\hat{\mathbf{j}}$  since the generalized forces, i.e. the external fields, are supposed to be classical. Thus the operator of the perturbation is of the type

$$\hat{V}(t) = e \int \hat{\mathbf{j}} \cdot \mathbf{A}(t) d^3\mathbf{r}. \quad (2.148)$$

We only consider the case that the system is homogeneous in space, then the integration in the above formula just gives

$$\hat{V}(t) = e\mathcal{V}\hat{\mathbf{j}} \cdot \mathbf{A}(t), \quad (2.149)$$

where  $\mathcal{V}$  is the volume of the system. And because the response current  $\mathbf{j}$  is in the direction of the generalized force  $\mathbf{A}$ , we can just concentrate on their component in that direction and write them as scalars  $j$  and  $A$ , i.e.

$$\hat{V}(t) = e\mathcal{V}\hat{j}A(t). \quad (2.150)$$

Let  $\alpha(\omega)$  denote the generalized susceptibility to  $A$  corresponding to the response  $-ej$ , i.e.,

$$-ej_\omega = \alpha(\omega)A_\omega, \quad (2.151)$$

---

<sup>5</sup>Here  $x$  is the electricity current density  $-e\mathbf{j}$  and the generalized force  $f$  is  $\mathbf{A}$ , thus  $-xf$  is  $e\mathbf{j} \cdot \mathbf{A}$ .

and denote the energy change rate of the system by  $Q$ . Then according to the fluctuation-dissipation theorem when the system is under a purely monochromatic magnetic potential  $A(t) = \frac{1}{2}A_0(e^{-i\omega t} + e^{i\omega t})$  we have

$$Q = \frac{1}{2}\mathcal{V}\omega\alpha''(\omega)|A_0|^2. \quad (2.152)$$

Now assume that all electrons are independent of each other, and such assumption is called the independent-particle approximation. Since the perturbation operator of a single electron is  $-evA$ , where  $v$  is the component of  $\mathbf{v}$  which is in the direction of  $\mathbf{j}$  and  $\mathbf{A}$ , applying Fermi's golden rule we find an expression for  $Q$  as

$$\begin{aligned} Q &= \frac{\pi e^2}{2\hbar^2} \sum_{nm} \hbar\omega_{mn} f_n(1-f_m) |v_{mn}|^2 |A_0|^2 [\delta(\omega + \omega_{nm}) + \delta(\omega + \omega_{mn})] \\ &= \frac{\pi e^2}{2\hbar} \sum_{nm} \omega_{mn} [f_n(1-f_m) - f_m(1-f_n)] |v_{mn}|^2 |A_0|^2 \delta(\omega + \omega_{nm}) \\ &= \frac{\pi e^2}{2\hbar} \sum_{nm} \omega (f_n - f_m) |v_{mn}|^2 |A_0|^2 \delta(\omega + \omega_{nm}), \end{aligned} \quad (2.153)$$

where  $\omega_{mn} = (\varepsilon_m - \varepsilon_n)/\hbar$ . The function  $f_n$  is just the Fermi distribution, and the factor  $f_n(1-f_m)$  is due to Pauli exclusion principle for a fermion: the electron transits from an occupied state  $n$  to an unoccupied state  $m$ . In the second step we interchanged the indices  $m$  and  $n$  in the summation of second delta function. Comparing this formula with (2.152) we find

$$\alpha''(\omega) = \frac{1}{\mathcal{V}} \frac{\pi e^2}{\hbar} \sum_{mn} (f_n - f_m) |v_{mn}|^2 \delta(\omega + \omega_{nm}). \quad (2.154)$$

However, this  $\alpha$  is not the electrical conductivity  $\sigma$ , and we need to express  $Q$  in terms of  $\sigma$ . To do so, we notice that the relation between the electric field  $E$  and magnetic vector  $A$  is just (here  $E$  is the component of electric field  $\mathbf{E}$  with the same direction of  $\mathbf{A}$ )

$$E(t) = -\frac{\partial A(t)}{\partial t}, \quad (2.155)$$

and after Fourier transformation we obtain

$$E_\omega = i\omega A_\omega. \quad (2.156)$$

Substituting this formula into (2.151) we have

$$-ej_\omega = \frac{\alpha(\omega)}{i\omega} E_\omega, \quad (2.157)$$

then according to the definition of the electrical conductivity,

$$\sigma(\omega) = \frac{\alpha(\omega)}{i\omega}. \quad (2.158)$$

Separating the real and imaginary parts of  $\sigma$  and  $\alpha$  gives

$$\alpha'(\omega) = -\omega\sigma''(\omega), \quad \alpha''(\omega) = \omega\sigma', \quad (2.159)$$

where  $\sigma'$  and  $\sigma''$  are real and imaginary parts of  $\sigma$  respectively.

Combining (2.152) and (2.158) an expression for  $Q$  in terms of  $E$  and  $\sigma$  is obtained as

$$Q = \frac{1}{2} \mathcal{V} \sigma'(\omega) |E_0|^2, \quad (2.160)$$

and this is exactly the *Joule heating* formula; and there is also an expression for  $\sigma'$  as

$$\sigma'(\omega) = \frac{\alpha''(\omega)}{\omega} = \frac{\pi e^2}{\mathcal{V}\omega} \sum_{mn} (f_n - f_m) |v_{mn}|^2 \delta(\hbar\omega + \hbar\omega_{nm}), \quad (2.161)$$

or, writing  $\hbar\omega_{nm} = \varepsilon_n - \varepsilon_m$ ,

$$\sigma'(\omega) = \frac{\pi e^2 \hbar}{\mathcal{V}} \sum_{mn} \frac{f_n - f_m}{\hbar\omega} |v_{mn}|^2 \delta(\varepsilon_n - \varepsilon_m + \hbar\omega). \quad (2.162)$$

This formula is called the *Kubo-Greenwood formula* [38–40], which is originally due to Ryogo Kubo and D. A. Greenwood. This form of Kubo-Greenwood formula contains a delta function which is not convenient to evaluate, so usually we write the formula in terms of Green's function. To do so, we first note that

$$\frac{f_n - f_m}{\hbar\omega} \delta(\varepsilon_n - \varepsilon_m + \hbar\omega) = \int \frac{f(\varepsilon) - f(\varepsilon + \hbar\omega)}{\hbar\omega} \delta(\varepsilon - \varepsilon_n) \delta(\varepsilon - \varepsilon_m + \hbar\omega) d\varepsilon, \quad (2.163)$$

hence  $\sigma'$  can be written as

$$\begin{aligned}
\sigma'(\omega) &= \frac{\pi e^2 \hbar}{\mathcal{V}} \int \sum_{mn} \left[ \frac{f(\varepsilon) - f(\varepsilon + \hbar\omega)}{\hbar\omega} v_{mn} v_{nm} \delta(\varepsilon - \varepsilon_n) \delta(\varepsilon - \varepsilon_m + \hbar\omega) \right] d\varepsilon \\
&= \frac{\pi e^2 \hbar}{\mathcal{V}} \int \frac{f(\varepsilon) - f(\varepsilon + \hbar\omega)}{\hbar\omega} \sum_{mn} v_{mn} \delta(\varepsilon - \varepsilon_n) v_{nm} \delta(\varepsilon - \varepsilon_m + \hbar\omega) d\varepsilon \\
&= \frac{\pi e^2 \hbar}{\mathcal{V}} \int \frac{f(\varepsilon) - f(\varepsilon + \hbar\omega)}{\hbar\omega} \text{Tr} \left[ \hat{v} \delta(\varepsilon - \hat{H}) \hat{v} \delta(\varepsilon + \hbar\omega - \hat{H}) \right] d\varepsilon.
\end{aligned} \tag{2.164}$$

The operator  $\delta(\varepsilon - \hat{H})$  represents the density of states at energy  $\varepsilon$  and  $\hat{H}$  is the Hamiltonian of a single electron, and it is related to the Green's function by

$$\delta(\varepsilon - \hat{H}) = -\frac{1}{\pi} \text{Im} G^R(\varepsilon) = \frac{1}{\pi} \text{Im} G^A = \frac{i}{2\pi} [G^R(\varepsilon) - G^A(\varepsilon)], \tag{2.165}$$

where  $G^R$  and  $G^A$  are retarded and advanced Green's function respectively. Therefore we reach the Kubo-Greenwood formula in terms of retarded Green's function as

$$\sigma'(\omega) = \frac{e^2 \hbar}{\pi \mathcal{V}} \int \frac{f(\varepsilon) - f(\varepsilon + \hbar\omega)}{\hbar\omega} \text{Tr} \left[ \hat{v} \text{Im} G^R(\varepsilon) \hat{v} \text{Im} G^R(\varepsilon + \hbar\omega) \right] d\varepsilon. \tag{2.166}$$

We often want the static conductivity  $\sigma(0) = \sigma'(0)$ , thus

$$\begin{aligned}
\sigma(0) &= \frac{e^2 \hbar}{\pi \mathcal{V}} \lim_{\omega \rightarrow 0} \int \frac{f(\varepsilon) - f(\varepsilon + \hbar\omega)}{\hbar\omega} \text{Tr} \left[ \hat{v} \text{Im} G^R(\varepsilon) \hat{v} \text{Im} G^R(\varepsilon + \hbar\omega) \right] d\varepsilon \\
&= \frac{e^2 \hbar}{\pi \mathcal{V}} \int \left( -\frac{\partial f}{\partial \varepsilon} \right) \text{Tr} \left[ \hat{v} \text{Im} G^R(\varepsilon) \hat{v} \text{Im} G^R(\varepsilon) \right] d\varepsilon.
\end{aligned} \tag{2.167}$$

Sometimes we can obtain an approximate  $\mathbf{k}$  independent self-energy  $\Sigma^R(\varepsilon)$  for retarded Green's function. For instance, coherent potential approximation and dynamical mean field theory would give such self-energy. In this case,  $G^R$  and  $\mathbf{v}$  are both diagonal in  $\mathbf{k}$ -representation, then we have

$$G^R(\varepsilon, \mathbf{k}) = \frac{1}{\varepsilon - \Sigma^R - \varepsilon_0(\mathbf{k})}, \quad \langle \mathbf{k} | \mathbf{v} | \mathbf{k} \rangle = \frac{1}{\hbar} \frac{\partial \varepsilon_0(\mathbf{k})}{\partial \mathbf{k}}, \tag{2.168}$$

and the formula for  $\sigma(0)$  becomes

$$\sigma(0) = 2 \frac{e^2 \hbar}{\pi \mathcal{V}} \int \left( -\frac{\partial f}{\partial \varepsilon} \right) \sum_{\mathbf{k}} |\langle \mathbf{k} | \hat{v} | \mathbf{k} \rangle|^2 |\text{Im} G^R(\varepsilon, \mathbf{k})|^2 d\varepsilon, \tag{2.169}$$

here  $v$  is the component of  $\mathbf{v}$  which is in the same direction of electric field  $\mathbf{E}$ , and the extra factor 2 is due to electron spin degeneracy. This formula has a similar form to Boltzmann's equation (2.91), this makes a connection between Kubo-Greenwood formula and Boltzmann equation. This connection was noticed by David Thouless [41] in 1975.

## 2.8 The Green-Kubo Formula

Usually when mentioning linear response theory, we actually refer to the *Green-Kubo formula*. It is a general quantum mechanical formula for the response coefficients (the generalized susceptibility) based on the first order perturbation, this is also the reason why this theory is called the *linear response* theory. This formula is due to Melville Green in 1954 [42] and Ryogo Kubo in 1957 [38].

We still write the operator of the perturbation in the form

$$\hat{V}(t) = -\hat{x}f(t), \quad (2.170)$$

where  $x$  is the physical quantity concerned and  $f(t)$  is a purely monochromatic function with a frequency  $\omega$ :

$$f(t) = \frac{1}{2}(f_0 e^{-i\omega t} + f_0^* e^{i\omega t}). \quad (2.171)$$

Let  $\Psi_n^{(0)}$  be the wave function of state  $n$  with eigenenergy  $E_n$  of the unperturbed system, then according to the time dependent perturbation theory we seek the perturbed wave function of state  $n$  in the first approximation as

$$\Psi_n = \Psi_n^{(0)} + \sum_m a_{mn} \Psi_m^{(0)}. \quad (2.172)$$

According to (2.46) the coefficients  $a_{mn}$  satisfy the equations

$$i\hbar \frac{da_{mn}}{dt} = V_{mn} e^{i\omega_{mn}t} = -\frac{1}{2} x_{mn} e^{i\omega_{mn}t} (f_0 e^{-i\omega t} + f_0^* e^{i\omega t}), \quad (2.173)$$

note that  $V_{mn}$  stands for  $\langle m | \hat{V}(t) | n \rangle$  which also depends on time. Like in time dependent perturbation theory, we assume the perturbation is “adiabatic switch-on” from  $t = -\infty$ ; this means that we need to put  $\omega \rightarrow \omega \mp i0$  in the factors  $e^{\pm i\omega t}$  (where  $i0$  denotes an infinitesimal  $i\eta$  with  $\eta \rightarrow 0$ ).

Then

$$\begin{aligned}
a_{mn}(t) &= \frac{i}{2\hbar} \int_{-\infty}^t x_{mn} e^{i\omega_{mn}\tau} \left[ f_0 e^{-i(\omega+i0)\tau} + f_0^* e^{i(\omega-i0)\tau} \right] d\tau \\
&= \frac{i}{2\hbar} \int_{-\infty}^t x_{mn} \left[ f_0 e^{i(\omega_{mn}-\omega-i0)\tau} + f_0^* e^{i(\omega_{mn}+\omega-i0)\tau} \right] d\tau \\
&= \frac{1}{2\hbar} x_{mn} e^{i\omega_{mn}t} \left[ \frac{f_0 e^{-i\omega t}}{\omega_{mn} - \omega - i0} + \frac{f_0^* e^{i\omega t}}{\omega_{mn} + \omega - i0} \right].
\end{aligned} \tag{2.174}$$

Suppose the system is in a canonical distribution with distribution function  $\rho_n = e^{(F-E_n)/T}$ , where  $F$  is the free energy of the system. Assume the mean value of  $x$  to be zero without perturbation, i.e.  $\sum_n \rho_n \langle \Psi_n^{(0)} | \hat{x} | \Psi_n^{(0)} \rangle = 0$ , then the mean value  $\bar{x}$  with perturbation is calculated in first approximation via

$$\begin{aligned}
\bar{x}(t) &= \sum_n \rho_n \langle \Psi_n | \hat{x} | \Psi_n \rangle \\
&= \sum_{mn} \rho_n (a_{mn} x_{nm} e^{i\omega_{nm}t} + a_{mn}^* x_{mn} e^{i\omega_{mn}t}) \\
&= \frac{1}{2\hbar} \sum_{mn} \rho_n x_{mn} x_{nm} \left[ \frac{1}{\omega_{mn} - \omega - i0} + \frac{1}{\omega_{mn} + \omega + i0} \right] f_0 e^{-i\omega t} + \text{c.c.},
\end{aligned} \tag{2.175}$$

where ‘‘c.c.’’ means complex conjugate. Comparing this formula with the expression (2.114) we find an expression for the generalized susceptibility  $\alpha(\omega)$  as

$$\alpha(\omega) = \frac{1}{\hbar} \sum_{mn} \rho_n |x_{mn}|^2 \left[ \frac{1}{\omega_{mn} - \omega - i0} + \frac{1}{\omega_{mn} + \omega + i0} \right]. \tag{2.176}$$

The real and imaginary parts of this expression can be separated by the formula of Cauchy principal value

$$\frac{1}{x \pm i0} = P \frac{1}{x} \mp i\pi\delta(x). \tag{2.177}$$

From this formula it is easy to see that  $\alpha''(\omega)$  recovers the expression in fluctuation-dissipation theorem.

The formula (2.176) is just the Fourier transform of the function

$$\alpha(t) = \frac{i}{\hbar} \theta(t) \langle \hat{x}(t) \hat{x}(0) - \hat{x}(0) \hat{x}(t) \rangle, \tag{2.178}$$

where the averaging is with respect to the equilibrium state (without perturbation) of the system



and  $\theta(t)$  is the Heaviside step function defined as

$$\theta(t) = \begin{cases} 1, & t > 0; \\ 0, & t < 0. \end{cases} \quad (2.179)$$

To see this, write (2.178) with respect to  $n$  state of the unperturbed system and we shall obtain that for  $t > 0$

$$\begin{aligned} \alpha(t) &= \frac{i}{\hbar} \sum_{mn} \rho_n [x_{nm} x_{mn} e^{i\omega_{nm}t} - x_{nm} x_{mn} e^{i\omega_{mn}t}] \\ &= \frac{i}{\hbar} \sum_{mn} \rho_n |x_{mn}|^2 [e^{i\omega_{nm}t} - e^{i\omega_{mn}t}], \end{aligned} \quad (2.180)$$

note that the factor  $e^{i\omega_{nm}t} - e^{i\omega_{mn}t}$  is purely imaginary, this ensures that  $\alpha(t)$  is real. Since  $\alpha(t)$  is zero except  $t > 0$ , the Fourier transform of  $e^{i\omega_{mn}t}$  is calculated as

$$\int_0^\infty e^{i\omega_{mn}t} e^{i(\omega+i0)t} dt = \frac{i}{\omega_{mn} + \omega + i0}. \quad (2.181)$$

Recalling that  $\omega_{mn} = -\omega_{nm}$ , we get the final result

$$\alpha(\omega) = \frac{i}{\hbar} \int_0^\infty \langle \hat{x}(t) \hat{x}(0) - \hat{x}(0) \hat{x}(t) \rangle e^{i\omega t} dt, \quad (2.182)$$

this formula is known as the Green-Kubo formula. It can be seen that the Green-Kubo formula relates the response coefficients to the equilibrium properties of the system.

The Green-Kubo formula is also related to the retarded Green's function in a simple manner. The usual definition of the retarded Green's function  $G^R(t)$  for  $x$  is

$$G^R(t) = -\frac{i}{\hbar} \theta(t) \langle \hat{x}(t) \hat{x}(0) - \hat{x}(0) \hat{x}(t) \rangle, \quad G^R(\omega) = \int_{-\infty}^\infty G^R(t) e^{i\omega t} dt, \quad (2.183)$$

therefore  $\alpha(\omega)$  is just the opposite of  $G^R(\omega)$ :

$$\alpha(\omega) = -G^R(\omega). \quad (2.184)$$

Similarly, when there are multiple variables  $x_i$ , the Green-Kubo formula for the generalized

susceptibility  $\alpha_{ik}(\omega)$  is given by

$$\alpha_{ik}(\omega) = \frac{i}{\hbar} \int_0^\infty \langle \hat{x}_i(t) \hat{x}_k(0) - \hat{x}_k(0) \hat{x}_i(t) \rangle e^{i\omega t} dt. \quad (2.185)$$

With the definition of the retarded Green's function

$$G_{ik}^R(t) = -\frac{i}{\hbar} \theta(t) \langle \hat{x}_i(t) \hat{x}_k(0) - \hat{x}_k(0) \hat{x}_i(t) \rangle, \quad G_{ik}^R(\omega) = \int_{-\infty}^\infty G_{ik}^R(t) e^{i\omega t} dt, \quad (2.186)$$

we can just write

$$\alpha_{ik}(\omega) = -G_{ik}^R(\omega). \quad (2.187)$$

## Kubo Identity

With the aid of *Kubo identity* [22] the Green-Kubo formula can be written in another form. The Kubo identity states that for a physical operator  $\hat{x}$  and a given Hamiltonian  $\hat{H}$  there is

$$[e^{-\beta\hat{H}}, \hat{x}] = e^{-\beta\hat{H}} \int_0^\beta e^{\lambda\hat{H}} [\hat{x}, \hat{H}] e^{-\lambda\hat{H}} d\lambda, \quad (2.188)$$

where  $[\hat{x}, \hat{H}]$  is the commutator and  $\beta = 1/T$ . To prove this relation, let us consider an operator

$$\hat{S}(\lambda) = e^{\lambda\hat{H}} [\hat{x}, e^{-\lambda\hat{H}}] = e^{\lambda\hat{H}} \hat{x} e^{-\lambda\hat{H}} - \hat{x}. \quad (2.189)$$

Differentiating this operator with respect to  $\lambda$  yields

$$\frac{d\hat{S}}{d\lambda} = e^{\lambda\hat{H}} \hat{H} \hat{x} e^{-\lambda\hat{H}} - e^{\lambda\hat{H}} \hat{x} \hat{H} e^{-\lambda\hat{H}} = e^{\lambda\hat{H}} [\hat{H}, \hat{x}] e^{-\lambda\hat{H}}. \quad (2.190)$$

Therefore

$$\hat{S}(\beta) = \hat{S}(0) + \int_0^\beta \frac{d\hat{S}}{d\lambda} d\lambda = \int_0^\beta e^{\lambda\hat{H}} [\hat{H}, \hat{x}] e^{-\lambda\hat{H}} d\lambda, \quad (2.191)$$

and finally we have

$$[e^{-\beta\hat{H}}, \hat{x}] = -e^{-\beta\hat{H}} \hat{S}(\beta) = e^{-\beta\hat{H}} \int_0^\beta e^{\lambda\hat{H}} [\hat{x}, \hat{H}] e^{-\lambda\hat{H}} d\lambda. \quad (2.192)$$

Now we write the distribution function  $\rho_n$  in its operator form, i.e., write it as the density matrix  $\hat{\rho} = e^{-\beta(F-\hat{H})}$ . Then according to Green-Kubo formula,

$$\begin{aligned}\alpha_{ik}(t) &= \frac{i}{\hbar}\theta(t)\langle\hat{x}_i(t)\hat{x}_k(0) - \hat{x}_k(0)\hat{x}_i(t)\rangle \\ &= \frac{i}{\hbar}\theta(t)\text{Tr}[\hat{\rho}\hat{x}_i(t)\hat{x}_k(0) - \hat{\rho}\hat{x}_k(0)\hat{x}_i(t)] \\ &= \frac{i}{\hbar}\theta(t)\text{Tr}\{\hat{x}_i(t)[\hat{x}_k(0)\hat{\rho} - \hat{\rho}\hat{x}_k(0)]\},\end{aligned}\tag{2.193}$$

here we have used the property that the trace is invariant under cyclic permutations. Substituting Kubo identity

$$[\hat{x}_k(0)\hat{\rho} - \hat{\rho}\hat{x}_k(0)] = \hat{\rho}\int_0^\beta e^{\lambda\hat{H}}[\hat{H}, \hat{x}_k(0)]e^{-\lambda\hat{H}}d\lambda\tag{2.194}$$

we obtain

$$\alpha_{ik}(t) = \frac{i}{\hbar}\theta(t)\int_0^\beta\text{Tr}\{\hat{x}_i(t)\hat{\rho}e^{\lambda\hat{H}}[\hat{H}, \hat{x}_k(0)]e^{-\lambda\hat{H}}\}d\lambda.\tag{2.195}$$

Recalling the Heisenberg equation for  $\hat{x}_k$

$$\dot{\hat{x}}_k = \frac{i}{\hbar}[\hat{H}, \hat{x}_k],\tag{2.196}$$

then we have

$$\begin{aligned}\alpha_{ik}(t) &= \theta(t)\int_0^\beta\text{Tr}\left[\hat{x}_i(t)\hat{\rho}e^{\lambda\hat{H}}\hat{x}_k(0)e^{-\lambda\hat{H}}\right]d\lambda \\ &= \theta(t)\int_0^\beta\text{Tr}\left[\hat{\rho}e^{\lambda\hat{H}}\hat{x}_k(0)e^{-\lambda\hat{H}}\hat{x}_i(t)\right]d\lambda \\ &= \theta(t)\int_0^\beta\langle e^{\lambda\hat{H}}\hat{x}_k(0)e^{-\lambda\hat{H}}\hat{x}_i(t)\rangle d\lambda.\end{aligned}\tag{2.197}$$

## 2.9 The Green-Kubo Formula for Electrical Conductivity

When deriving the Kubo-Greenwood formula we only considered a special case that the current is homogeneous in space and always in the same direction of external field, the fluctuations of the current in space are totally neglected. Now let us consider a more general case.

The presence of the external field  $\mathbf{A}(t, \mathbf{r})$  induces an electricity current  $-e\mathbf{j}(t, \mathbf{r})$ . The generalized susceptibility of  $-e\mathbf{j}(t, \mathbf{r})$  corresponding to  $\mathbf{A}(t, \mathbf{r})$  is defined as

$$-ej_a(t, \mathbf{r}) = \int_0^\infty d\tau \int d^3\mathbf{r}' \sum_b \alpha_{ab}(\tau; \mathbf{r}, \mathbf{r}') A_b(t - \tau, \mathbf{r}'),\tag{2.198}$$

where  $a, b = x, y, z$  are the spatial components. We can also define a conductivity as the response coefficients to  $\mathbf{E}(t, \mathbf{r})$  as

$$-ej_a(t, \mathbf{r}) = \int_0^\infty d\tau \int d^3\mathbf{r}' \sum_b \sigma_{ab}(\tau; \mathbf{r}, \mathbf{r}') E_b(t - \tau, \mathbf{r}'). \quad (2.199)$$

The operator of the perturbation is written in terms of  $\mathbf{A}(t, \mathbf{r})$  as

$$\hat{V}(t) = e \int \sum_a \hat{j}_a(t, \mathbf{r}) A_a(t, \mathbf{r}) d^3\mathbf{r}. \quad (2.200)$$

According to Green-Kubo formula we immediately obtain

$$\alpha_{ab}(t; \mathbf{r}, \mathbf{r}') d^3\mathbf{r}' = \frac{i}{\hbar} \langle [-e\hat{j}_a(t, \mathbf{r}), -e\hat{j}_b(0, \mathbf{r}') d^3\mathbf{r}'] \rangle, \quad t > 0; \quad (2.201)$$

i.e.,

$$\alpha_{ab}(t; \mathbf{r}, \mathbf{r}') = \frac{ie^2}{\hbar} \langle [\hat{j}_a(t, \mathbf{r}), \hat{j}_b(0, \mathbf{r}')] \rangle, \quad t > 0. \quad (2.202)$$

Its Fourier component is written as

$$\alpha_{ab}(\omega; \mathbf{r}, \mathbf{r}') = \frac{ie^2}{\hbar} \int_0^\infty \langle [\hat{j}_a(t, \mathbf{r}), \hat{j}_b(0, \mathbf{r}')] \rangle e^{i\omega t} dt, \quad (2.203)$$

the relation between  $\alpha(\omega; \mathbf{r}, \mathbf{r}')$  and  $\sigma(\omega; \mathbf{r}, \mathbf{r}')$  is similar with (2.158) and thus we have

$$\sigma_{ab}(\omega; \mathbf{r}, \mathbf{r}') = \frac{e^2}{\hbar\omega} \int_0^\infty \langle [\hat{j}_a(t, \mathbf{r}), \hat{j}_b(0, \mathbf{r}')] \rangle e^{i\omega t} dt. \quad (2.204)$$

This formula is often referred to as the *Kubo formula of conductivity*. Now assume  $\sigma_{ab}(\omega; \mathbf{r}, \mathbf{r}')$  is only a function of the position separation  $\sigma(\omega, \mathbf{r} - \mathbf{r}')$ . This assumption is incorrect on an atomic scale, but it is permissible in solids when the current is to be averaged over many unit cells of the

solid. Then the formula can be written in  $\mathbf{k}$ -representation as

$$\begin{aligned}\sigma_{ab}(\omega, \mathbf{k}) &= \frac{e^2}{\hbar\omega} \int \int_0^\infty \langle [\hat{j}_a(t, \mathbf{r}), \hat{j}_b(0, \mathbf{r}')] \rangle e^{i\omega t} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} dt d^3(\mathbf{r}-\mathbf{r}') \\ &= \frac{e^2}{\hbar\omega} \int \int_0^\infty \langle [\hat{j}_a(t, \mathbf{r}), \hat{j}_b(0, \mathbf{r}')] \rangle e^{i\omega t} e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} dt d^3\mathbf{r} \\ &= \frac{e^2}{\hbar\omega} e^{i\mathbf{k}\cdot\mathbf{r}'} \int_0^\infty \langle [\hat{j}_a(t, \mathbf{k}), \hat{j}_b(0, \mathbf{r}')] \rangle e^{i\omega t} dt,\end{aligned}\tag{2.205}$$

with the definition of Fourier transform

$$\hat{j}(t, \mathbf{k}) = \int \hat{j}(t, \mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} d^3\mathbf{r}.\tag{2.206}$$

However, this result is not quite right. We need to average over the space variable  $\mathbf{r}'$  in order to eliminate atomic fluctuations. This average is done by an integration  $\frac{1}{\mathcal{V}} \int d^3\mathbf{r}'$ : integrate over all volume and then divide by  $\mathcal{V}$ . The only  $\mathbf{r}'$  dependent factor in the expression is  $e^{i\mathbf{k}\cdot\mathbf{r}'} \hat{j}_b(0, \mathbf{r}')$ , after the integration it becomes

$$\frac{1}{\mathcal{V}} \int \hat{j}_b(0, \mathbf{r}') e^{i\mathbf{k}\cdot\mathbf{r}'} d^3\mathbf{r}' = \frac{1}{\mathcal{V}} \hat{j}_b(0, -\mathbf{k}) = \frac{1}{\mathcal{V}} \hat{j}_b^\dagger(0, \mathbf{k}).\tag{2.207}$$

Thus the final result is

$$\sigma_{ab}(\omega, \mathbf{k}) = \frac{e^2}{\hbar\omega\mathcal{V}} \int_0^\infty \langle [\hat{j}_a(t, \mathbf{k}), \hat{j}_b^\dagger(0, \mathbf{k})] \rangle e^{i\omega t} dt,\tag{2.208}$$

this is the Kubo formula in  $\mathbf{k}$ -representation.

However, this conductivity is not the usual electrical conductivity  $\sigma_{ab}(t)$  or  $\sigma_{ab}(\omega)$ , and it can be seen from the fact that its dimension is not correct. To find the usual electrical conductivity, the mean current density  $-e\bar{j}_a(t)$  averaging over the volume is need. According to (2.199) we have

$$-e\bar{j}_a(t) = -\frac{e}{\mathcal{V}} \int j_a(t, \mathbf{r}) d^3\mathbf{r} = \frac{1}{\mathcal{V}} \int_0^\infty d\tau \int d^3\mathbf{r} d^3\mathbf{r}' \sum_b \sigma_{ab}(\tau; \mathbf{r}, \mathbf{r}') E_b(t-\tau, \mathbf{r}'),\tag{2.209}$$

therefore

$$\sigma_{ab}(\omega) = \frac{1}{\mathcal{V}} \int d^3\mathbf{r} d^3\mathbf{r}' \sigma_{ab}(\omega; \mathbf{r}, \mathbf{r}').\tag{2.210}$$

If  $\sigma_{ab}(\omega; \mathbf{r}, \mathbf{r}')$  is only a function of the position separation  $\sigma(\omega, \mathbf{r}-\mathbf{r}')$ , the integral over  $\int d^3\mathbf{r} d^3\mathbf{r}'$

can be written as  $\mathcal{V} \int d^3(\mathbf{r} - \mathbf{r}')$ , then

$$\sigma_{ab}(\omega) = \int \sigma_{ab}(\omega, \mathbf{r}) d^3 \mathbf{r}. \quad (2.211)$$

Now we can write the expression for electrical conductivity in terms of operator  $\hat{j}_a$  explicitly as

$$\sigma_{ab}(\omega) = \frac{e^2}{\hbar\omega} \int \int_0^\infty \langle [\hat{j}_a(t, \mathbf{r}), \hat{j}_b(0, 0)] \rangle e^{i\omega t} dt d^3 \mathbf{r}, \quad (2.212)$$

or

$$\sigma_{ab}(\omega) = \frac{e^2}{\hbar\omega} \lim_{\mathbf{k} \rightarrow 0} \int \int_0^\infty \langle [\hat{j}_a(t, \mathbf{r}), \hat{j}_b(0, 0)] \rangle e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} dt d^3 \mathbf{r}, \quad (2.213)$$

where the limit  $\mathbf{k} \rightarrow 0$  corresponds to the *hydrodynamic approximation* [24], under such approximation only long wavelength (small  $\mathbf{k}$ ) excitations are studied and the atomic fluctuations are ignored.

## The Formula for Thermoelectric Coefficient

The electric field can also induce heat current. According to the discussion in section 2.4, the corresponding response coefficient to electric field  $\mathbf{E}$  is a combination of conductivity, Seebeck coefficient and temperature  $\sigma ST$ . So we have

$$(q - \mu j)_a(t; \mathbf{r}, \mathbf{r}') = \int_0^\infty d\tau \int d^3 \mathbf{r}' \sum_b (\sigma ST)_{ab}(\tau; \mathbf{r}, \mathbf{r}') E_b(t - \tau, \mathbf{r}'). \quad (2.214)$$

It is easy to write down a Kubo formula for  $\sigma ST$ . Since the operator of the perturbation remains the same, we need to only change the operator  $-e\hat{j}_a$  in the Kubo formula by  $(\hat{q} - \mu\hat{j})_a$ , then

$$(\sigma ST)_{ab}(\omega; \mathbf{r}, \mathbf{r}') = -\frac{e}{\hbar\omega} \int_0^\infty \langle [(\hat{q} - \mu\hat{j})_a(t, \mathbf{r}), \hat{j}_b^\dagger(0, \mathbf{r}')] \rangle e^{i\omega t} dt. \quad (2.215)$$

Similarly, under the assumption that  $\sigma ST$  is a function of position separation  $(\sigma ST)(\omega, \mathbf{r} - \mathbf{r}')$  we can obtain the formula in  $\mathbf{k}$ -representation as

$$(\sigma ST)_{ab}(\omega, \mathbf{k}) = -\frac{e}{\hbar\omega\mathcal{V}} \int_0^\infty \langle [(\hat{q} - \mu\hat{j})_a(t, \mathbf{k}), \hat{j}_b^\dagger(0, \mathbf{k})] \rangle e^{i\omega t} dt. \quad (2.216)$$

The dimension of  $(\sigma ST)_{ab}(t; \mathbf{r}, \mathbf{r}')$  is not the same as usual  $(\sigma ST)_{ab}$ , so we need to use hydrodynamic approximation again to get the formula after the space averaging as

$$(\sigma ST)_{ab}(\omega) = -\frac{e}{\hbar\omega} \lim_{\mathbf{k} \rightarrow 0} \int \int_0^\infty \langle [(\hat{q} - \mu\hat{j})_a(t, \mathbf{r}), \hat{j}_b(0, 0)] \rangle e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} dt d^3\mathbf{r}. \quad (2.217)$$

This formula allows us to calculate the combination quantity  $(\sigma ST)_{ab}$ , so together with the Kubo formula of conductivity we can get both the electrical conductivity and the Seebeck coefficient.

### Connection to Kubo-Greenwood Formula

The Green-Kubo formula is usually hard to evaluate, therefore we often approximate the electrons in solids as non interacting particles, which means that there exist single particle stationary states. Under such approximation the Green-Kubo formula reduces to Kubo-Greenwood formula [43] which is much easier to evaluate.

Now denote the wave function of a single electron in state  $n$  with eigenenergy  $\varepsilon_n$  by  $\psi_n(\mathbf{r})$ . Now we introduce the  $\psi$ -operators which are defined as

$$\hat{\psi}(\mathbf{r}) = \sum_n \psi_n(\mathbf{r}) \hat{c}_n, \quad \hat{\psi}^\dagger(\mathbf{r}) = \sum_n \psi_n^*(\mathbf{r}) \hat{c}_n^\dagger, \quad (2.218)$$

which would be more convenient here. With these operators the particle current operator  $\hat{\mathbf{j}}$  can be expressed as

$$\hat{\mathbf{j}}(\mathbf{r}) = \hat{\psi}^\dagger(\mathbf{r}) \hat{\mathbf{v}} \hat{\psi}(\mathbf{r}), \quad (2.219)$$

where  $\hat{\mathbf{v}}$  is the single particle velocity operator which acts only on the wave function on its right.

The wave function  $\psi_n(\mathbf{r})$  is normalized by condition

$$\int \psi_n^*(\mathbf{r}) \psi_n(\mathbf{r}) d^3\mathbf{r} = 1, \quad (2.220)$$

thus  $\hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r})$  is the particle number density operator at position  $\mathbf{r}$  and

$$\int \hat{\psi}^\dagger(\mathbf{r}) \hat{\psi}(\mathbf{r}) d^3\mathbf{r} = \sum_n \hat{c}_n^\dagger \hat{c}_n = \hat{N} \quad (2.221)$$

is the particle number operator. With these operators the conductivity formula (2.210) writes

$$\sigma_{ab}(\omega) = \frac{e^2}{\hbar\omega\mathcal{V}} \int \int_0^\infty \langle [e^{\frac{i}{\hbar}\hat{H}t} \hat{\psi}^\dagger(\mathbf{r}) \hat{v}_a \hat{\psi}(\mathbf{r}) e^{-\frac{i}{\hbar}\hat{H}t}, \hat{\psi}^\dagger(\mathbf{r}') \hat{v}_b \hat{\psi}(\mathbf{r}')] \rangle e^{i\omega t} dt d^3\mathbf{r} d^3\mathbf{r}', \quad (2.222)$$

or explicitly in terms of  $\hat{c}_n^\dagger$  and  $\hat{c}_n$ ,

$$\sigma_{ab}(\omega) = \frac{e^2}{\hbar\omega\mathcal{V}} \int_0^\infty \sum_{nm,pq} \langle [(v_a)_{nm} \hat{c}_n^\dagger \hat{c}_m e^{i\omega_{nm}t}, (v_b)_{pq} \hat{c}_p^\dagger \hat{c}_q] \rangle e^{i\omega t} dt, \quad (2.223)$$

where

$$(v_a)_{nm} = \int \psi_n(\mathbf{r}) \hat{v}_a \psi_m(\mathbf{r}) d^3\mathbf{r}, \quad (v_b)_{pq} = \int \psi_p(\mathbf{r}') \hat{v}_b \psi_q(\mathbf{r}') d^3\mathbf{r}', \quad \omega_{nm} = (\varepsilon_n - \varepsilon_m)/\hbar. \quad (2.224)$$

To evaluate the above formula we need the expression for  $\langle \hat{c}_n^\dagger \hat{c}_m \hat{c}_p^\dagger \hat{c}_q \rangle$ . Since electrons are fermion, according to Wick's theorem we have

$$\begin{aligned} \langle \hat{c}_n^\dagger \hat{c}_m \hat{c}_p^\dagger \hat{c}_q \rangle &= \langle \hat{c}_n^\dagger \hat{c}_m \rangle \langle \hat{c}_p^\dagger \hat{c}_q \rangle + \langle \hat{c}_n^\dagger \hat{c}_q \rangle \langle \hat{c}_m \hat{c}_p^\dagger \rangle \\ &= \delta_{mn} \delta_{pq} f_n f_p + \delta_{nq} \delta_{mp} f_n (1 - f_m), \end{aligned} \quad (2.225)$$

where  $f_n$  is the Fermi distribution function. Accordingly,

$$\langle [\hat{c}_n^\dagger \hat{c}_m, \hat{c}_p^\dagger \hat{c}_q] \rangle = \delta_{nq} \delta_{mp} (f_n - f_m), \quad (2.226)$$

and this expression leads us to

$$\sigma_{ab}(\omega) = \frac{ie^2}{\mathcal{V}} \sum_{mn} \frac{f_n - f_m}{\hbar\omega} \frac{(v_a)_{nm} (v_b)_{mn}}{\omega_{nm} + \omega + i0}. \quad (2.227)$$

The real and imaginary parts of this expression can be separated by Cauchy principal value formula

$$\frac{1}{x \pm i0} = P \frac{1}{x} \mp i\pi\delta(x). \quad (2.228)$$



Thus we obtain the formula for the real part of  $\sigma_{ab}(\omega)$ :

$$\text{Re } \sigma_{ab}(\omega) = \frac{\pi e^2 \hbar}{\mathcal{V}} \sum_{mn} \frac{f_n - f_m}{\hbar \omega} (v_a)_{nm} (v_b)_{mn} \delta(\varepsilon_n - \varepsilon_m + \hbar \omega). \quad (2.229)$$

This formula coincides with the Kubo-Greenwood formula introduced in an earlier section but is in a more general manner: the possibility that the electricity current might not be parallel to the electric field is taken into account, so the conductivity is a tensor. Thus we reach a conclusion that the Kubo-Greenwood formula is an approximation of the Green-Kubo formula where the interaction between electrons is ignored. This is just the independent particle approximation.

Similarly, if written in terms of the retarded Green's function, the formula is

$$\text{Re } \sigma_{ab}(\omega) = \frac{e^2 \hbar}{\pi \mathcal{V}} \int \frac{f(\varepsilon) - f(\varepsilon + \hbar \omega)}{\hbar \omega} \text{Tr} [\hat{v}_a \text{Im } G^R(\varepsilon) \hat{v}_b \text{Im } G^R(\varepsilon + \hbar \omega)] d\varepsilon, \quad (2.230)$$

and the static formula is just

$$\sigma_{ab}(0) = \text{Re } \sigma_{ab}(0) = \frac{e^2 \hbar}{\pi \mathcal{V}} \int \left( -\frac{\partial f}{\partial \varepsilon} \right) \text{Tr} [\hat{v}_a \text{Im } G^R(\varepsilon) \hat{v}_b \text{Im } G^R(\varepsilon)] d\varepsilon. \quad (2.231)$$

If the Green's function and velocity are both diagonal in the  $\mathbf{k}$ -representation, then the static formula is written as

$$\sigma(0) = 2 \frac{e^2 \hbar}{\pi \mathcal{V}} \int \left( -\frac{\partial f}{\partial \varepsilon} \right) \sum_{\mathbf{k}} v_a(\mathbf{k}) v_b(\mathbf{k}) |\text{Im } G(\varepsilon, \mathbf{k})|^2 d\varepsilon, \quad (2.232)$$

where the factor 2 is due to electron spin degeneracy.

Starting from Green-Kubo formula, we can also obtain a Kubo-Greenwood formula for the thermoelectric coefficient  $\sigma_{ST}$ . With independent particle approximation, the heat current density  $\mathbf{q} - \mu \mathbf{j}$  is usually written as  $(\varepsilon - \mu) \mathbf{j}$ . Following the same procedures above the Kubo-Greenwood formula for  $\sigma_{ST}$  is obtained as

$$(\sigma_{ST})_{ab}(\omega) = -\frac{\pi e \hbar}{\mathcal{V}} \sum_{mn} \frac{f_n - f_m}{\hbar \omega} (\varepsilon_n - \mu) (v_a)_{nm} (v_b)_{mn} \delta(\varepsilon_n - \varepsilon_m + \hbar \omega). \quad (2.233)$$

Write it in terms of the Green's function, then

$$\text{Re}(\sigma ST)_{ab}(\omega) = -\frac{e\hbar}{\pi\mathcal{V}} \int \frac{f(\varepsilon) - f(\varepsilon + \hbar\omega)}{\hbar\omega} \text{Tr}[(\varepsilon - \mu)\hat{v}_a \text{Im} G^R(\varepsilon)\hat{v}_b \text{Im} G^R(\varepsilon + \hbar\omega)] d\varepsilon, \quad (2.234)$$

and the static formula is

$$(\sigma ST)_{ab}(0) = \text{Re}(\sigma ST)_{ab}(0) = -\frac{e\hbar}{\pi\mathcal{V}} \int \left(-\frac{\partial f}{\partial \varepsilon}\right) \text{Tr}[(\varepsilon - \mu)\hat{v}_a \text{Im} G^R(\varepsilon)\hat{v}_b \text{Im} G^R(\varepsilon)] d\varepsilon. \quad (2.235)$$

And the formula in the  $\mathbf{k}$ -representation is

$$(\sigma ST)_{ab}(0) = -2\frac{e\hbar}{\pi\mathcal{V}} \int \left(-\frac{\partial f}{\partial \varepsilon}\right) \sum_{\mathbf{k}} (\varepsilon - \mu)v_a(\mathbf{k})v_b(\mathbf{k}) |\text{Im} G^R(\varepsilon, \mathbf{k})|^2 d\varepsilon. \quad (2.236)$$

## 2.10 Non-Equilibrium Green's Function Formalism

Non-equilibrium Green's function formalism [31, 44–47] provides a general way which in principle can handle not only equilibrium states but also any non-equilibrium states. This is the reason why it is called the *non-equilibrium Green's function*. It should be emphasized that this formalism, although it is called non-equilibrium Green's function, is also suitable for equilibrium states. In this section we shall briefly review this formalism. In particular, we shall discuss the fluctuation-dissipation theorem in terms of non-equilibrium Green's function formalism.

Suppose there are several physical operators  $\hat{x}_i, \hat{x}_k$  under consideration. As we know, when dealing with the system at zero temperature, one usually uses time ordered Green's functions which are defined as

$$G_{ik}(t, t') = -\frac{i}{\hbar} \langle 0 | T \hat{x}_i(t) \hat{x}_k(t') | 0 \rangle, \quad (2.237)$$

where  $\hat{x}_i(t), \hat{x}_k(t')$  are operators in Heisenberg picture. The angle brackets  $\langle 0 | \dots | 0 \rangle$  denote averaging over the ground state of the system. The symbol  $T$  denotes the chronological product (time ordering operator): the operators following it are arranged from right to left in order of increasing time. For fermionic operators, the interchange of operators must change the sign of the product,

while for bosonic operators the sign remains unchanged. Explicitly,

$$i\hbar G_{ik}(t, t') = \begin{cases} \langle 0 | \hat{x}_i(t) \hat{x}_k(t') | 0 \rangle, & t > t'; \\ \mp \langle 0 | \hat{x}_k(t') \hat{x}_i(t) | 0 \rangle, & t < t'. \end{cases} \quad (2.238)$$

The upper sign refers to fermionic operators and the lower sign to bosonic operators. When only the ground state is considered, this time ordered Green's function is enough to apply perturbation method, and the reason is the following: when the Green's function is changed into interaction picture, the perturbation is usually assumed under an ‘‘adiabatic switch-on’’ and then ‘‘adiabatic switch-off’’, and after such procedure the system would return to the ground state and just leave an unimportant phase factor.

As applied to finite temperature case or non-equilibrium case, the Green's function is defined in the same manner:

$$G_{ik}(t, t') = -\frac{i}{\hbar} \langle T \hat{x}_i(t) \hat{x}_k(t') \rangle. \quad (2.239)$$

The only difference is that the averaging (denoted by  $\langle \dots \rangle$ ) is now over any state of the system, not necessarily over only the ground state of the system.

However, considering only time ordered Green's functions is not enough to apply the perturbation method, and we must introduce other Green's functions. First let us denote the time ordered Green's function (2.239) by  $G_{ik}^{--}$ , and define it as

$$i\hbar G_{ik}^{--}(t, t') = \langle T \hat{x}_i(t) \hat{x}_k(t') \rangle = \begin{cases} \langle \hat{x}_i(t) \hat{x}_k(t') \rangle, & t > t'; \\ \mp \langle \hat{x}_k(t') \hat{x}_i(t) \rangle, & t < t'. \end{cases} \quad (2.240)$$

Then we define another Green's function

$$i\hbar G_{ik}^{++}(t, t') = \langle \bar{T} \hat{x}_i(t) \hat{x}_k(t') \rangle = \begin{cases} \mp \langle \hat{x}_k(t') \hat{x}_i(t) \rangle, & t > t'; \\ \langle \hat{x}_i(t) \hat{x}_k(t') \rangle, & t < t', \end{cases} \quad (2.241)$$

which differs from  $G^{--}$  that  $T$  is replaced by  $\bar{T}$ . The symbol  $\bar{T}$  signifies that the operator factors are arranged in the reverse of chronological order, it is called anti-time ordering operator.

Two further Green's functions are defined without time ordering  $T$  or anti-time ordering oper-

ator  $\bar{T}$  as

$$i\hbar G_{ik}^{+-}(t, t') = \langle \hat{x}_i(t) \hat{x}_k(t') \rangle, \quad i\hbar G_{ik}^{-+}(t, t') = \mp \langle \hat{x}_k(t') \hat{x}_i(t) \rangle. \quad (2.242)$$

The upper sign refers to fermionic operators and the lower sign to bosonic operators, in the following we shall always use this convention.

The four Green's functions thus defined are not independent of each other. It is easy to see that they are related by a linear relation:

$$G^{--} + G^{++} = G^{-+} + G^{+-}. \quad (2.243)$$

The relation between these new defined Green's functions and the retarded and advanced Green's functions is important. Recalling the definitions of retarded and advanced Green's functions

$$i\hbar G_{ik}^R(t, t') = \begin{cases} \langle \hat{x}_i(t) \hat{x}_k(t') \pm \hat{x}_k(t') \hat{x}_i(t) \rangle, & t > t'; \\ 0, & t < t'; \end{cases} \quad (2.244)$$

$$i\hbar G_{ik}^A(t, t') = \begin{cases} 0, & t > t'; \\ -\langle \hat{x}_i(t) \hat{x}_k(t') \pm \hat{x}_k(t') \hat{x}_i(t) \rangle, & t < t', \end{cases} \quad (2.245)$$

and a direct comparison to those new defined functions gives

$$\begin{cases} G^R = G^{--} - G^{-+} = G^{+-} - G^{++}, \\ G^A = G^{--} - G^{+-} = G^{-+} - G^{++}. \end{cases} \quad (2.246)$$

Instead of  $G^{+-}$  and  $G^{-+}$ , sometimes more common notations  $G^>$  and  $G^<$  are used that

$$G^> = G^{+-}, \quad G^< = G^{-+}. \quad (2.247)$$

These new defined functions constitute non-equilibrium Green's function (NEGF) formalism.

## Fluctuation-Dissipation Theorem in Terms of Non-Equilibrium Green's Function

With the definitions of these non-equilibrium Green's functions, the fluctuation-dissipation theorem can be written in another form. Let us consider the system which is time transitional invariant and

is in canonical equilibrium. And several observable variables  $x_i, x_k$  are under consideration. Note that since  $x_i, x_k$  are observable variables, the corresponding operators  $\hat{x}_i, \hat{x}_k$  are bosonic. Using the previous definitions it is easy to write the quantum correlation function for  $\hat{x}_i, \hat{x}_k$  as

$$\phi_{ik}(t) = \frac{1}{2} \langle \hat{x}_i(t) \hat{x}_k(0) + \hat{x}_k(0) \hat{x}_i(t) \rangle = \frac{i\hbar}{2} [G_{ik}^{+-}(t) + G_{ik}^{-+}(t)], \quad (2.248)$$

and its Fourier component as

$$\phi_{ik}(\omega) = \frac{i\hbar}{2} [G_{ik}^{+-}(\omega) + G_{ik}^{-+}(\omega)], \quad (2.249)$$

where

$$G_{ik}^{+-}(\omega) = \int_{-\infty}^{\infty} G_{ik}^{+-}(t) e^{i\omega t} dt, \quad G_{ik}^{-+}(\omega) = \int_{-\infty}^{\infty} G_{ik}^{-+}(t) e^{i\omega t} dt. \quad (2.250)$$

According to Green-Kubo formula, the generalized susceptibility  $\alpha$  is just the opposite of the retarded Green's function  $G^R$ :

$$\alpha_{ik}(\omega) = -G_{ik}^R(\omega), \quad G_{ik}^R(\omega) = \int_0^{\infty} G_{ik}^R(t) e^{i\omega t} dt. \quad (2.251)$$

Therefore the fluctuation-dissipation theorem for multiple variables (2.146) can be written as

$$[G_{ik}^{+-}(\omega) + G_{ik}^{-+}(\omega)] = [G_{ik}^R(\omega) - G_{ki}^{R*}(\omega)] \coth \frac{\hbar\omega}{2T}. \quad (2.252)$$

As will be shown later,  $G_{ik}^{R*}(\omega) = G_{ik}^A(\omega)$ , so we can write this expression as

$$[G_{ik}^{+-}(\omega) + G_{ik}^{-+}(\omega)] = [G_{ik}^R(\omega) - G_{ki}^A(\omega)] \coth \frac{\hbar\omega}{2T}. \quad (2.253)$$

This formula indicates that the fluctuation-dissipation theorem is essentially the relation between different Green's functions in equilibrium. In fact, the formula (2.146) is just a special case at which only bosonic operators are considered and an auxiliary perturbation is needed. Now using non-equilibrium Green's function formalism we can derive a more general fluctuation-dissipation theorem.

The fluctuation-dissipation theorem is for Green's function in equilibrium, and time transitional

invariance is also assumed. The definition of the retarded Green's function then is (the upper sign is for fermionic operators and the lower sign is for bosonic operators)

$$G_{ik}^R(t) = -\frac{i}{\hbar}\theta(t)\langle\hat{x}_i(t)\hat{x}_k(0) \pm \hat{x}_k(0)\hat{x}_i(t)\rangle, \quad (2.254)$$

and its Fourier transform is

$$G_{ik}^R(\omega) = -\frac{i}{\hbar}\int_0^\infty\langle\hat{x}_i(t)\hat{x}_k(0) \pm \hat{x}_k(0)\hat{x}_i(t)\rangle e^{i\omega t} dt. \quad (2.255)$$

Let  $\rho_n$  denote the canonical distribution function  $e^{(F-E_n)/T}$ , where  $F$  is the free energy of the system and  $E_n$  is the eigenenergy of the system in eigenstate  $n$ . Then we can write  $G_{ik}^R(t)$  explicitly as

$$G_{ik}^R(t) = -\frac{i}{\hbar}\theta(t)\sum_{nm}\rho_n[(x_i)_{nm}(x_k)_{mn}e^{i\omega_{nm}t} \pm (x_k)_{nm}(x_i)_{mn}e^{i\omega_{mn}t}], \quad (2.256)$$

where  $\omega_{mn} = (E_m - E_n)/\hbar$  and  $(x_i)_{nm}$  stands for  $\langle n|\hat{x}_i|m\rangle$ . Hence its Fourier transform  $G_{ik}^R(\omega)$  is

$$\begin{aligned} G_{ik}^R(\omega) &= -\frac{i}{\hbar}\int_0^\infty\sum_{nm}\rho_n[(x_i)_{nm}(x_k)_{mn}e^{i(\omega_{nm}+\omega)t} \pm (x_k)_{nm}(x_i)_{mn}e^{i(\omega_{mn}+\omega)t}]dt \\ &= \frac{1}{\hbar}\sum_{nm}\rho_n\left[\frac{(x_i)_{nm}(x_k)_{mn}}{\omega_{nm} + \omega + i0} \pm \frac{(x_k)_{nm}(x_i)_{mn}}{\omega_{mn} + \omega + i0}\right]. \end{aligned} \quad (2.257)$$

This kind of expression of the Green's function is called the *Lehmann representation*. Similarly, we can also write  $G_{ik}^A(t)$  as

$$G_{ik}^A(t) = \frac{i}{\hbar}\theta(-t)\sum_{nm}\rho_n[(x_i)_{nm}(x_k)_{mn}e^{i\omega_{nm}t} \pm (x_k)_{nm}(x_i)_{mn}e^{i\omega_{mn}t}], \quad (2.258)$$

and its Lehmann representation is

$$\begin{aligned} G_{ik}^A(\omega) &= \frac{i}{\hbar}\int_{-\infty}^0\sum_{nm}\rho_n[(x_i)_{nm}(x_k)_{mn}e^{i(\omega_{nm}+\omega)t} \pm (x_k)_{nm}(x_i)_{mn}e^{i(\omega_{mn}+\omega)t}]dt \\ &= \frac{1}{\hbar}\sum_{nm}\rho_n\left[\frac{(x_i)_{nm}(x_k)_{mn}}{\omega_{nm} + \omega - i0} \pm \frac{(x_k)_{nm}(x_i)_{mn}}{\omega_{mn} + \omega - i0}\right]. \end{aligned} \quad (2.259)$$

Note that we must add an infinitesimal  $-i0$  into  $\omega$  when integrating from  $-\infty$  to 0 to ensure the

convergence, that is

$$\int_{-\infty}^0 e^{i\omega t} dt = \int_{-\infty}^0 e^{i(\omega-i0)t} dt = \frac{-i}{\omega - i0}. \quad (2.260)$$

A comparison of (2.257) and (2.259) shows

$$G_{ik}^{R*}(\omega) = G_{ik}^A(\omega). \quad (2.261)$$

The real and imaginary parts of  $G_{ik}^R(\omega)$  and  $G_{ik}^A(\omega)$  can be separated by Cauchy principal value formula

$$\frac{1}{x \pm i0} = P \frac{1}{x} \mp i\pi\delta(x). \quad (2.262)$$

Since  $G_{ik}^A(\omega)$  is just the complex conjugate of  $G_{ik}^R(\omega)$  here we only show the results of  $G_{ik}^R(\omega)$ :

$$\left\{ \begin{array}{l} \text{Re } G_{ik}^R(\omega) = \frac{1}{\hbar} P \sum_{nm} \rho_n \left[ \frac{(x_i)_{nm}(x_k)_{mn}}{\omega_{nm} + \omega} \pm \frac{(x_k)_{nm}(x_i)_{mn}}{\omega_{mn} + \omega} \right], \\ \text{Im } G_{ik}^R(\omega) = -\frac{\pi}{\hbar} \sum_{nm} \rho_n [(x_i)_{nm}(x_k)_{mn}\delta(\omega_{nm} + \omega) \pm (x_k)_{nm}(x_i)_{mn}\delta(\omega_{mn} + \omega)]. \end{array} \right. \quad (2.263)$$

Exchange the indices  $m, n$  of the second term in the summation,  $\text{Im } G_{ik}^R(\omega)$  can be also written as

$$\begin{aligned} \text{Im } G_{ik}^R(\omega) &= -\frac{\pi}{\hbar} \sum_{nm} (\rho_n \pm \rho_m) (x_i)_{nm} (x_k)_{mn} \delta(\omega_{nm} + \omega) \\ &= -\frac{\pi}{\hbar} \sum_{nm} \rho_n (1 \pm e^{-\hbar\omega/T}) (x_i)_{nm} (x_k)_{mn} \delta(\omega_{nm} + \omega). \end{aligned} \quad (2.264)$$

It can be seen from (2.263) that  $\text{Re } G_{ik}^R(\omega)$  and  $\text{Im } G_{ik}^R(\omega)$  are related by

$$\text{Re } G_{ik}^R(\omega) = -\frac{1}{\pi} P \int \frac{\text{Im } G_{ik}^R(\xi)}{\omega - \xi} d\xi, \quad (2.265)$$

this is also called the *Kramers-Kronig relation*. It may also be noted that this relation allows us to write

$$G_{ik}^R(\omega) = -\frac{1}{\pi} \int \frac{\text{Im } G_{ik}^R(\xi)}{\omega - \xi + i0} d\xi. \quad (2.266)$$

Similarly, in equilibrium state we can write down the Lehmann representation for  $G_{ik}^{+-}$  and  $G_{ik}^{-+}$ :

$$\begin{aligned}
G_{ik}^{+-}(\omega) &= -\frac{i}{\hbar} \int_{-\infty}^{\infty} \sum_{nm} \rho_n(x_i)_{nm}(x_k)_{mn} e^{i(\omega_{nm}+\omega)t} dt \\
&= -\frac{2\pi i}{\hbar} \sum_{nm} \rho_n(x_i)_{nm}(x_k)_{mn} \delta(\omega_{nm} + \omega),
\end{aligned} \tag{2.267}$$

and

$$\begin{aligned}
G_{ik}^{-+}(\omega) &= \pm \frac{i}{\hbar} \int_{-\infty}^{\infty} \sum_{nm} \rho_n(x_k)_{nm}(x_i)_{mn} e^{i(\omega_{mn}+\omega)t} dt \\
&= \pm \frac{2\pi i}{\hbar} \sum_{nm} \rho_n(x_k)_{nm}(x_i)_{mn} \delta(\omega_{mn} + \omega).
\end{aligned} \tag{2.268}$$

Note here we have used the formula for  $\delta$  function that

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ipx} dp = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-ipx} dp. \tag{2.269}$$

Therefore we can write the sum of  $G_{ik}^{+-}(\omega)$  and  $G_{ik}^{-+}$  as

$$\begin{aligned}
G_{ik}^{+-}(\omega) + G_{ik}^{-+}(\omega) &= -\frac{2\pi i}{\hbar} \sum_{nm} \rho_n [(x_i)_{nm}(x_k)_{mn} \delta(\omega_{nm} + \omega) \mp (x_k)_{nm}(x_i)_{mn} \delta(\omega_{mn} + \omega)] \\
&= -\frac{2\pi i}{\hbar} \sum_{nm} (\rho_n \mp \rho_m) (x_i)_{nm}(x_k)_{mn} \delta(\omega_{nm} + \omega) \\
&= -\frac{2\pi i}{\hbar} \sum_{nm} \rho_n (1 \mp e^{-\hbar\omega/T}) (x_i)_{nm}(x_k)_{mn} \delta(\omega_{nm} + \omega).
\end{aligned} \tag{2.270}$$

Comparing (2.270) with (2.264), it is clear that

$$[G_{ik}^{+-}(\omega) + G_{ik}^{-+}(\omega)] = 2i \operatorname{Im} G_{ik}^R(\omega) \frac{1 \mp e^{-\hbar\omega/T}}{1 \pm e^{-\hbar\omega/T}}, \tag{2.271}$$

or

$$[G_{ik}^{+-}(\omega) + G_{ik}^{-+}(\omega)] = [G_{ik}^R - G_{ki}^A] \frac{1 \mp e^{-\hbar\omega/T}}{1 \pm e^{-\hbar\omega/T}}. \tag{2.272}$$

Therefore for fermionic operators we have

$$[G_{ik}^{+-}(\omega) + G_{ik}^{-+}(\omega)] = [G_{ik}^R - G_{ki}^A] \tanh \frac{\hbar\omega}{2T}, \tag{2.273}$$



and for bosonic operators

$$[G_{ik}^{+-}(\omega) + G_{ik}^{-+}(\omega)] = [G_{ik}^R - G_{ki}^A] \coth \frac{\hbar\omega}{2T}. \quad (2.274)$$

Comparing (2.264) and (2.267) we can also find the relationship between  $\text{Im } G_{ik}^R(\omega)$  and  $G_{ik}^{+-}(\omega)$ :

$$G_{ik}^R(\omega) - G_{ik}^A(\omega) = G_{ik}^{+-}(\omega)(1 \pm e^{-\hbar\omega/T}), \quad (2.275)$$

thus we can express the average quantity  $\langle \hat{x}_i \hat{x}_k \rangle$  by the inverse Fourier transform at  $t = 0$ :

$$\langle \hat{x}_i \hat{x}_k \rangle = i\hbar \lim_{t \rightarrow 0} \int G_{ik}^{+-}(\omega) e^{-i\omega t} \frac{d\omega}{2\pi} = -\frac{\hbar}{\pi} \int \frac{\text{Im } G_{ik}^R(\omega)}{1 \pm e^{-\hbar\omega/T}} d\omega. \quad (2.276)$$

This formula is usually called the *spectrum theorem* of the Green's function, and it is also treated as a part of the fluctuation-dissipation theorem. Similarly, interchanging the indices  $m, n$  in (2.268) and recalling that  $\rho_n = \rho_m e^{-\hbar\omega_{nm}/T}$  we find the relation between  $G_{ik}^{+-}(\omega)$  and  $G_{ik}^{-+}(\omega)$  as [48]

$$G_{ik}^{+-}(\omega) = \mp e^{\hbar\omega/T} G_{ik}^{-+}(\omega). \quad (2.277)$$

When the fluctuation-dissipation theorem is written in non-equilibrium Green's function formalism, its physical meaning is not so clear: the fluctuation and dissipation processes are not pointed out explicitly. What's more, when operators are fermionic they do not correspond to any observable quantity, thus there is no corresponding actual physical process explicitly. However, this form of the fluctuation-dissipation theorem reveals a more profound mathematical relationship between the different Green's functions. This kind of relationship is the internal property of the system in equilibrium, and is much more general than (2.146).

## 2.11 Fluctuations

In the previous sections we have discussed the Green-Kubo formula whose derivation is based on time dependent perturbation theory. To apply perturbation theory, we need to assume an external field and a corresponding perturbation operator  $\hat{x}f$  in the Hamiltonian. If the perturbation is an electric field, then according to Green-Kubo formula we can obtain the electricity and heat currents

as responses to electric field. However, we do not know whether there is a Green-Kubo formula for heat conductivity yet: because it is the response coefficient to the temperature gradient, thus there is no external field acting as perturbation in the Hamiltonian and the time dependent perturbation theory is not applicable here<sup>6</sup>. Does a Green-Kubo formula for heat conductivity exist? The answer is yes, but it can not be derived from perturbation theory directly since temperature gradient is not an external perturbation but a statistical inhomogeneity of the system. In this section we shall discuss the general fluctuation theory as prior knowledge of the derivation of the Green-Kubo formula for heat conductivity.

### Gaussian Distribution

According to the definition, let  $\Omega$  be the statistical weight, then the entropy can be written as

$$S = \ln \Omega. \quad (2.278)$$

As we know, in the microcanonical ensemble the probability distribution  $w$  is proportional to the statistical weight  $\Omega$ , thus we can write

$$w \propto e^S. \quad (2.279)$$

Let us consider a system with several thermodynamic quantities  $x_1, \dots, x_n$  under consideration. It will be convenient to suppose that the mean value  $\bar{x}_i$  has already been subtracted from  $x_i$ , so we shall assume that  $\bar{x}_i = 0$ . We now write the entropy  $S$  formally as a function of all these thermodynamic quantities  $S(x_1, \dots, x_n)$ , then the probability density function  $w(x_1, \dots, x_n)$  is accordingly

$$w(x_1, \dots, x_n) \propto e^{S(x_1, \dots, x_n)}, \quad (2.280)$$

with the normalization condition

$$\int w(x_1, \dots, x_n) dx_1 \cdots dx_n = 1. \quad (2.281)$$

The entropy  $S$  has a maximum when  $x_i = \bar{x}_i = 0$ , hence  $\partial S / \partial x_i = 0$  and the matrix  $\partial^2 S / \partial x_i \partial x_k$

---

<sup>6</sup>However, Joaquin Luttinger [51] gave a “mechanical” derivation for Green-Kubo formula. That is, the derivation still depends on perturbation theory but it needs some tricks.

is negative definite for  $(x_1, \dots, x_n) = 0$ . In fluctuations, the quantities  $x_1, \dots, x_n$  are supposed to be small, so expanding  $S$  in powers of  $x_1, \dots, x_n$  and retaining terms of up to the second order yields

$$S(x_1, \dots, x_n) = S_0 - \frac{1}{2} \sum_{i,k=1}^n \beta_{ik} x_i x_k, \quad (2.282)$$

where  $\beta_{ik}$  is a positive definite matrix, and clearly  $\beta_{ik} = \beta_{ki}$ . In the rest of the section we shall omit the summation sign, and all repeated indices imply the summation from 1 to  $n$ . Thus we write

$$S = S_0 - \frac{1}{2} \beta_{ik} x_i x_k. \quad (2.283)$$

Substituting this expression into (2.280), the probability density  $w$  is written as a *Gaussian distribution*

$$w = A e^{-\frac{1}{2} \beta_{ik} x_i x_k}. \quad (2.284)$$

The constant  $A$  is determined by the normalization condition (2.281), according to the properties of the Gaussian distribution we have

$$A = \frac{\sqrt{\beta}}{(2\pi)^{\frac{n}{2}}}, \quad (2.285)$$

where  $\beta = |\beta_{ik}|$  is the determinant of the matrix  $\beta_{ik}$ . Then the Gaussian distribution expression for  $w$  is

$$w = \frac{\sqrt{\beta}}{(2\pi)^{\frac{n}{2}}} \exp\left(-\frac{1}{2} \beta_{ik} x_i x_k\right). \quad (2.286)$$

Now define the quantity

$$X_i = -\frac{\partial S}{\partial x_i} = \beta_{ik} x_k, \quad (2.287)$$

which is referred as *thermodynamically conjugate* [32, 52] to  $x_i$ . Note that this conjugacy is reciprocal: according to the definition we also have  $x_i = -\partial S / \partial X_i$  since

$$dS = -X_k dx_k = -\beta_{ki} x_i dx_k = -x_i d(\beta_{ik} x_k) = -x_i dX_i. \quad (2.288)$$

Now let us determine the mean values  $\langle x_i X_k \rangle$ :

$$\langle x_i X_k \rangle = \frac{\sqrt{\beta}}{(2\pi)^{\frac{n}{2}}} \int x_i X_k \exp\left(-\frac{1}{2} \beta_{ik} x_i x_k\right) dx_1 \cdots dx_n. \quad (2.289)$$

To calculate this integral, let us first assume for the moment that  $\bar{x}_i$  are not zero, and according to the definition of the mean values

$$\bar{x}_i = \frac{\sqrt{\beta}}{(2\pi)^{\frac{n}{2}}} \int \cdots \int x_i \exp \left[ -\frac{1}{2} \beta_{ik} (x_i - \bar{x}_i)(x_k - \bar{x}_k) \right] dx_1 \cdots dx_n. \quad (2.290)$$

Differentiating both sides of this equation with respect to  $\bar{x}_k$  gives

$$\delta_{ik} = \frac{\sqrt{\beta}}{(2\pi)^{\frac{n}{2}}} \int \cdots \int x_i \beta_{kl} (x_l - \bar{x}_l) \exp \left[ -\frac{1}{2} \beta_{ik} (x_i - \bar{x}_i)(x_k - \bar{x}_k) \right] dx_1 \cdots dx_n, \quad (2.291)$$

and putting all the  $\bar{x}_i$  equal to zero again we obtain that

$$\delta_{ik} = \frac{\sqrt{\beta}}{(2\pi)^{\frac{n}{2}}} \int \cdots \int x_i \beta_{kl} x_l \exp \left( -\frac{1}{2} \beta_{ik} x_i x_k \right) dx_1 \cdots dx_n. \quad (2.292)$$

From this equation it is easy to see that

$$\beta_{kl} \langle x_i x_l \rangle = \delta_{ik}, \quad (2.293)$$

or

$$\langle x_i x_k \rangle = \beta_{ik}^{-1}, \quad (2.294)$$

where  $\beta_{ik}^{-1}$  is an element of the matrix inverse to  $\beta_{ik}$ . Substituting  $X_k = \beta_{kl} x_l$  into (2.293) we finally get

$$\langle x_i X_k \rangle = \delta_{ik}. \quad (2.295)$$

We can also determine the mean value  $\langle X_i X_k \rangle$  by writing it as

$$\langle X_i X_k \rangle = \beta_{il} \langle x_l X_k \rangle = \beta_{il} \delta_{lk}, \quad (2.296)$$

i.e.,

$$\langle X_i X_k \rangle = \beta_{ik}. \quad (2.297)$$

We can also express the time derivative of the entropy in terms of  $x_i$  and  $X_i$  as

$$\dot{S} = -\beta_{ik} \dot{x}_i x_k = -\dot{x}_i X_i. \quad (2.298)$$

## 2.12 Onsager's Principle

If at some instant the value of a physical quantity  $x$  is large compared to the mean fluctuation, i.e. the system is far from equilibrium, then the system will tend to reach the equilibrium state and  $x$  will tend to reach its mean value  $\bar{x}$ . Here we shall put  $\bar{x} = 0$  and the rate of change of  $x$  is determined by the value of  $x$  itself:  $\dot{x} = \dot{x}(x)$ . If  $x$  is still small comparing with the whole system, then  $\dot{x}$  can be expanded in powers of  $x$ , keeping only the linear term we have

$$\frac{dx}{dt} = -\lambda x, \quad (2.299)$$

where  $\lambda$  is a positive constant. There is no zero order term in this expression, since the rate of change  $\dot{x}$  must be zero in equilibrium, i.e. at  $x = 0$ .

The equation (2.299) gives the “damping” term for  $x$  when it deviates from equilibrium value  $x = 0$ . However, due to the environment there also exist “heating” or “driving” terms which are usually called *random forces*. The random forces would “thermalize” the system and let the physical quantity  $x$  deviate from its mean value. Denoting the random force by  $y(t)$  and adding it to the right handed side of (2.299) we obtain

$$\frac{dx}{dt} = -\lambda x + y(t). \quad (2.300)$$

This equation is referred as *Langevin equation* [53]. Note that this Langevin equation is generalized in that it describes not the random movement of a particle but thermodynamic quantity  $x$ . And  $y(t)$  is supposed to be the source of the fluctuations of  $x$  and its mean value averaged over time is supposed to be zero. The Langevin equation can be also formulated with several physical quantities  $x_1, \dots, x_n$  as

$$\frac{dx_i}{dt} = -\lambda_{ik} x_k + y_i(t), \quad (2.301)$$

where  $\lambda_{ik}$  is a positive definite matrix.

Let us now turn to the relation between (2.301) and the correlation function. The correlation function  $\phi_{ik}(t)$  is defined as

$$\phi(t) = \langle x_i(t)x_k(0) \rangle. \quad (2.302)$$

Define a quantity  $\xi_i(t)$  as the mean value of  $x_i$  at a time  $t > 0$  with the condition that it had some given value  $x_i$  at the prior time  $t = 0$ . Thus the correlation function  $\phi_{ik}(t)$  can be written as

$$\phi_{ik}(t) = \langle \xi_i(t)x_k \rangle, \quad (2.303)$$

where the averaging is over the probabilities of various values of  $x_i, x_k$  at the initial time  $t = 0$ . Then the equation for  $\xi_i$  is just the average of (2.301):

$$\dot{\xi}_i = -\lambda_{ik}\xi_k, \quad (2.304)$$

where the random forces are averaged out. And the equation for the correlation function is thus

$$\frac{d\phi_{ik}(t)}{dt} = \langle \dot{\xi}_i(t)x_k \rangle = -\lambda_{il}\phi_{lk}(t), \quad t > 0. \quad (2.305)$$

To find  $\phi_{ik}(t)$  these equations are to be integrated with the initial conditions

$$\phi_{ik}(0) = \langle x_i(0)x_k(0) \rangle \equiv \langle x_i x_k \rangle = \beta_{ik}^{-1}, \quad (2.306)$$

where these initial conditions are from (2.294).

### The Symmetry of the Kinetic Coefficients

The equations (2.301) have a deep-lying internal symmetry, which becomes explicit when the right hand side is expressed in terms of the thermodynamic conjugate  $X_i$  of  $x_i$ . According to (2.287), we have

$$X_i = \beta_{ik}x_k. \quad (2.307)$$

Thus expressing the right hand side in terms of  $X_i$ , the equations (2.301) can be written as

$$\frac{dx_i}{dt} = -\gamma_{ik}X_k + y(t), \quad (2.308)$$

where

$$\gamma_{ik} = \lambda_{il}\beta_{lk}^{-1} \quad (2.309)$$

are new constants called *kinetic coefficients*. The response coefficients mentioned in previous sections, such as the electrical conductivity, are also particular examples of kinetic coefficients.

Define a quantity  $\Xi_i(t)$  as the mean value of  $X_i$  at a time  $t > 0$  with the initial condition that it has some given value  $X_i$  at the prior time  $t = 0$ . Then we can write the average of (2.308) as

$$\frac{d\xi_i(t)}{dt} = -\gamma_{ik}\Xi_k, \quad t > 0, \quad (2.310)$$

where the averages of random force  $y_i(t)$  are zero. The correlation function  $\phi_{ik}(t)$  has time reversal symmetry  $\phi_{ik}(t) = \phi_{ik}(-t)$ , which may be expressed as

$$\langle x_i(t)x_k(0) \rangle = \langle x_i(0)x_k(t) \rangle, \quad (2.311)$$

or, with  $\xi_i(t)$ ,

$$\langle \xi_i(t)x_k \rangle = \langle x_i\xi_k(t) \rangle, \quad (2.312)$$

where the averaging is with respect to the probabilities of the various values of all the  $x_i, x_k$  at  $t = 0$ . Differentiating this equation with respect to time  $t$  and substituting the derivatives  $\dot{\xi}_i$  from (2.310), we obtain that

$$\gamma_{il}\langle \Xi_l(t)x_k \rangle = \gamma_{kl}\langle x_i\Xi_k(t) \rangle. \quad (2.313)$$

When  $t = 0$ , the  $\Xi_l$  are equal to  $X_l(0)$ ; hence putting  $t = 0$  in the above equation we get

$$\gamma_{il}\langle X_lx_k \rangle = \gamma_{kl}\langle x_iX_k \rangle, \quad (2.314)$$

where these two averages are taken at the same time. According to (2.295), such mean values

$\langle x_l X_k \rangle = \delta_{lk}$ , thus we arrive at an important result

$$\gamma_{ik} = \gamma_{ki}. \quad (2.315)$$

This expression states that the kinetic coefficients are symmetric. Such symmetry is called *Onsager's principle* or *Onsager's relation*, which is due to Lars Onsager in 1931 [54].

The proof of the Onsager's principle is based on the time reversal symmetry of the correlation function  $\phi_{ik}$ , and an assumption has been made that the quantities  $x_i$  and  $x_k$  are not affected by time reversal. However, this is not always true. For instance, the velocity  $\mathbf{v}$  would become  $-\mathbf{v}$  under the time reversal. Thus if  $x_i$  and  $x_k$  both remain or change the sign, the relation (2.315) is still valid. But if one of  $x_i$  and  $x_k$  changes sign and the other remains unchanged, the Onsager's principle should be formulated as

$$\gamma_{ik} = -\gamma_{ki}. \quad (2.316)$$

What's more, angular momentum  $\boldsymbol{\Omega}$  and magnetic field  $\mathbf{B}$  change sign under time reversal. So the Onsager's principle when angular momentum is under consideration or the system is under a magnetic field are

$$\gamma_{ik}(\boldsymbol{\Omega}) = \gamma_{ki}(-\boldsymbol{\Omega}), \quad \gamma_{ik}(\mathbf{B}) = \gamma_{ki}(-\mathbf{B}). \quad (2.317)$$

Similarly we can define kinetic coefficients  $\zeta_{ik}$  in another form taking the derivatives of  $X_i$  as

$$\frac{dX_i(t)}{dt} = -\zeta_{ik}x_k + Y_i(t), \quad \zeta_{ik} = \beta_{il}\lambda_{lk}, \quad (2.318)$$

where  $Y_i(t)$  are the corresponding random forces. The coefficients  $\zeta_{ik}$  have similar symmetry properties to those of  $\gamma_{ik}$ . This can be derived following the same procedure and using the reciprocal relation between  $x_i$  and  $X_i$ .



### Relation Between Random Forces and Kinetic Coefficients

Let us return to equations (2.305) and try to express the solutions in terms of  $\lambda_{ik}$  and  $\beta_{ik}$ . We use a notation  $(x_i x_k)_\omega$  to denote the Fourier component of the correlation function, which is

$$(x_i x_k)_\omega = \int_{-\infty}^{\infty} \phi_{ik}(t) e^{i\omega t} dt \equiv \int_{-\infty}^{\infty} \langle x_i(t) x_k(0) \rangle e^{i\omega t} dt. \quad (2.319)$$

From the definition of  $\phi_{ik}$  there is an obvious symmetry  $\phi_{ik}(t) = \phi_{ki}(-t)$ . Note that this symmetry is just time transition invariance, not the time reversal symmetry  $\phi_{ik}(t) = \phi_{ik}(-t)$ . This symmetry shows that

$$(x_i x_k)_\omega = (x_k x_i)_{-\omega} = (x_k x_i)_\omega^*. \quad (2.320)$$

Since (2.305) refer only to times  $t > 0$ , we shall apply a “one-sided” Fourier transformation to it, multiplying by  $e^{i\omega t}$  and integrating with respect to  $t$  from 0 to  $\infty$ . The term  $\dot{\phi}_{ik}(t) e^{i\omega t}$  is integrated by parts, and since  $\phi_{ik}(\infty) = 0$  we have

$$\phi_{ik}(0) - i\omega (x_i x_k)_\omega^+ = -\lambda_{il} (x_l x_k)_\omega^+, \quad (2.321)$$

with the notation

$$(x_i x_k)_\omega^+ = \int_0^{\infty} \phi_{ik}(t) e^{i\omega t} dt. \quad (2.322)$$

The value of  $\phi_{ik}(0)$  is given by the initial condition (2.306); thus

$$(\lambda_{il} - i\omega \delta_{il}) (x_l x_k)_\omega^+ = \beta_{ik}^{-1}, \quad (2.323)$$

or

$$(\zeta_{il} - i\omega \beta_{il}) (x_l x_k)_\omega^+ = \delta_{ik}, \quad (2.324)$$

where the coefficients  $\lambda_{il}$  have been replaced by  $\zeta_{il} = \beta_{ik} \lambda_{kl}$ , which are more convenient here. The solution for these algebraic equations is

$$(x_l x_k)_\omega^+ = (\zeta - i\omega \beta)_{lk}^{-1}, \quad (2.325)$$

where the index  $-1$  means the inverse matrix.

On the other hand, according to the definition and the symmetry  $\phi_{ik}(t) = \phi_{ki}(-t)$ , the full  $(x_i x_k)_\omega$  can be expressed by “one-sided”  $(x_i x_k)_\omega$  as

$$(x_i x_k)_\omega = (x_i x_k)_\omega^+ + [(x_k x_i)_\omega^+]^*. \quad (2.326)$$

Thus finally we have

$$(x_i x_k)_\omega = (\zeta - i\omega\beta)_{ik}^{-1} + (\zeta + i\omega\beta)_{ki}^{-1}. \quad (2.327)$$

Using this result we can find the expression for the correlation function of random forces. For example, the Langevin equation for  $X_i$  with random forces  $Y_i$ , see (2.318), is

$$\dot{X}_i(t) = -\zeta_{ik} x_k + Y_i(t). \quad (2.328)$$

Applying a Fourier transformation on these equations gives

$$-i\omega X_{i\omega} + \zeta_{ik} x_{k\omega} = Y_{i\omega}, \quad (2.329)$$

where

$$X_{i\omega} = \int_{-\infty}^{\infty} X_i(t) e^{i\omega t} dt, \quad x_{k\omega} = \int_{-\infty}^{\infty} x_k(t) e^{i\omega t} dt, \quad Y_{i\omega} = \int_{-\infty}^{\infty} Y_i(t) e^{i\omega t} dt. \quad (2.330)$$

Or recalling that  $X_i = \beta_{ik} x_k$ , we have

$$(\zeta_{ik} - i\omega\beta_{ik}) x_{k\omega} = Y_{i\omega}. \quad (2.331)$$

Now write the correlation function of  $Y_i$  as  $\langle Y_i(t) Y_k(t') \rangle$ , then it can be written in inverse Fourier transformation form as

$$\langle Y_i(t) Y_k(t') \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle Y_{i\omega} Y_{k\omega'} \rangle e^{-i(\omega t + \omega' t')} \frac{d\omega d\omega'}{(2\pi)^2}. \quad (2.332)$$

Since  $\langle Y_i(t) Y_k(t') \rangle$  is a function only depends on  $t - t'$ , the integrand must contain a delta function

of  $\omega + \omega'$ , i.e.

$$\langle Y_{i\omega} Y_{k\omega'} \rangle = 2\pi (Y_i Y_k)_\omega \delta(\omega + \omega'), \quad (2.333)$$

where (because  $\langle Y_i(t) Y_k(t') \rangle$  only depends on  $t - t'$ , we can just replace it by  $\langle Y_i(t) Y_k(0) \rangle$ )

$$(Y_i Y_k)_\omega = \int_{-\infty}^{\infty} \langle Y_i(t) Y_k(0) \rangle e^{i\omega t} dt, \quad (2.334)$$

is the Fourier component of the correlation function  $\langle Y_i(t) Y_k(0) \rangle$ . Similarly, we have

$$\langle x_{i\omega} x_{k\omega'} \rangle = 2\pi (x_i x_k)_\omega \delta(\omega + \omega'), \quad (2.335)$$

where

$$(x_i x_k)_\omega = \int_{-\infty}^{\infty} \langle x_i(t) x_k(0) \rangle e^{i\omega t} dt. \quad (2.336)$$

Then from (2.331) it is easy to see that

$$\langle Y_{i\omega} Y_{k\omega'} \rangle = (\zeta_{il} - i\omega\beta_{il})(\zeta_{km} - i\omega'\beta_{km}) \langle x_{l\omega} x_{m\omega'} \rangle, \quad (2.337)$$

or, because of the delta function  $\delta(\omega + \omega')$  in  $\langle x_{i\omega} x_{k\omega'} \rangle$  and  $\langle Y_{i\omega} Y_{k\omega'} \rangle$ ,

$$(Y_i Y_k)_\omega = (\zeta_{il} - i\omega\beta_{il})(\zeta_{km} + i\omega\beta_{km}) (x_l x_m)_\omega. \quad (2.338)$$

Finally substituting (2.327) in the above formula gives

$$(Y_i Y_k)_\omega = \zeta_{ik} + \zeta_{ki}. \quad (2.339)$$

If we use random forces  $y_i$  in the Langevin equation

$$\dot{x}_i = -\gamma_{ik} X_k + y_i, \quad (2.340)$$

following the same procedure their correlation function is obtained that

$$(y_i y_k)_\omega = \gamma_{ik} + \gamma_{ki}, \quad (2.341)$$

where

$$(y_i y_k)_\omega = \int_{-\infty}^{\infty} \langle y_i(t) y_k(0) \rangle e^{i\omega t} dt. \quad (2.342)$$

All the above formulas are classical or quasi-classical, thus we need to find their corresponding quantum version. This correspondence is reached by writing the random forces in terms of the generalized forces and collaborating with the fluctuation-dissipation theorem. According to (2.147), the static susceptibility  $T\alpha_{ik}(0) = \frac{1}{2} \langle \hat{x}_i \hat{x}_k + \hat{x}_k \hat{x}_i \rangle$ , and its classical correspondence is just  $T\alpha_{ik}(0) = \langle x_i x_k \rangle$ , comparing it with (2.294) we find

$$T\alpha_{ik}(0) = \beta_{ik}^{-1}. \quad (2.343)$$

Now we assume that the system is subject to the external static forces  $f_i$ . This causes displacement of the equilibrium state, in which  $\bar{x}_i$  is now not zero but  $\alpha_{ik}(0)f_k = \beta_{ik}^{-1}f_k/T$ . Thus the equation of  $\dot{x}_i$  becomes

$$\dot{x}_i = -\lambda_{ik} [x_k - \alpha_{ik}(0)f_k], \quad (2.344)$$

which differs from (2.301) in that  $\dot{x}_i$  is not zero when  $x = 0$  but when  $x_i = \alpha_{ik}(0)f_k$ . In this equation we do not write the random forces  $y_i$  because  $f_k$  would be regarded as random forces. This equation may be regarded as valid also when the generalized forces are time-dependent  $f_k(t)$ , as long as the period of the forces  $f_k(t)$  is large compared with the relaxation time for the establishment of the partial equilibrium corresponding to any given value of thermodynamic quantities  $x_i$ .

The displacement may be also written in terms of  $\bar{X}_i$  by using

$$\bar{X}_i = \beta_{ik} \bar{x}_k = \beta_{ik} \alpha_{kl}(0) f_l(t) = \frac{f_i(t)}{T}, \quad (2.345)$$

therefore we have

$$\dot{x}_i = -\gamma_{ik} \left[ X_k - \frac{f_k(t)}{T} \right]. \quad (2.346)$$

Now we shall regard  $f_k(t)$  as random forces, and comparing with Langevin equation (2.308) immediately gives the relation between  $y_i$  and  $f_k$ :

$$y_i(t) = \frac{\gamma_{ik} f_k(t)}{T}. \quad (2.347)$$

Substituting  $f_k(t)$  and  $x_i(t)$  as the periodic functions (2.139) and (2.140) in (2.346) (with the  $X_k$  written as  $X_k = \beta_{kl}x_l$ ) and separating the terms in  $e^{-i\omega t}$  and  $e^{i\omega t}$ , we obtain

$$-i\omega\alpha_{im}(\omega)f_{0m} = -\gamma_{ik}\beta_{kl}\alpha_{lm}(\omega)f_{0m} + \frac{1}{T}\gamma_{im}f_{0m}. \quad (2.348)$$

Since  $f_{0m}$  are arbitrary, we have

$$-i\omega\alpha_{im}(\omega) + \gamma_{ik}\beta_{kl}\alpha_{lm} = \frac{1}{T}\gamma_{im}, \quad (2.349)$$

or

$$\alpha_{ik}(\omega) = \frac{1}{T}(\beta - i\omega\gamma^{-1})_{ik}^{-1}, \quad (2.350)$$

where the index  $-1$  means the inverse matrix. This gives the relation between the generalized susceptibility  $\alpha_{ik}(\omega)$  and the kinetic coefficients  $\gamma_{ik}$ .

According to the fluctuation-dissipation theorem (2.146) we have

$$(x_i x_k)_\omega = \frac{i}{2}\hbar[\alpha_{ki}^*(\omega) - \alpha_{ik}(\omega)] \coth \frac{\hbar\omega}{2T}, \quad (2.351)$$

where  $(x_i x_k)_\omega$  is the Fourier component of the quantum correlation function, i.e.

$$(x_i x_k)_\omega = \int_{-\infty}^{\infty} \frac{1}{2} \langle \hat{x}_i(t) \hat{x}_k(0) + \hat{x}_k(0) \hat{x}_i(t) \rangle e^{i\omega t} dt. \quad (2.352)$$

And according to the definition of the generalized susceptibility  $\alpha_{ik}(\omega)$ , we write

$$x_{i\omega} = \alpha_{ik}(\omega)f_k, \quad \text{or} \quad f_{i\omega} = \alpha_{ik}^{-1}x_{k\omega}. \quad (2.353)$$

From the above formula it is easy to see that

$$\begin{aligned} (f_i f_k)_\omega &= \alpha_{il}^{-1}(\omega)\alpha_{km}^{-1}(-\omega)(x_l x_m)_\omega \\ &= \alpha_{il}^{-1}\alpha_{km}^{-1*}(x_l x_m)_\omega \\ &= \frac{i}{2}\hbar(\alpha_{ik}^{-1} - \alpha_{ki}^{-1*}) \coth \frac{\hbar\omega}{2T}. \end{aligned} \quad (2.354)$$

Since  $\beta_{ik} = -\partial^2 S / \partial x_i \partial x_k = \beta_{ki}$ , substituting (2.350) in the above formula gives

$$(f_i f_k)_\omega = (\gamma_{ik}^{-1} + \gamma_{ki}^{-1}) \frac{\hbar\omega T}{2} \coth \frac{\hbar\omega}{2T}. \quad (2.355)$$

Using the relation (2.347) we finally obtain the quantum expression for  $(y_i y_k)_\omega$ :

$$(y_i y_k)_\omega = (\gamma_{ik} + \gamma_{ki}) \frac{\hbar\omega}{2T} \coth \frac{\hbar\omega}{2T}. \quad (2.356)$$

The quantum expression (2.356) differs from the classical one (2.341) by a factor

$$\frac{\hbar\omega}{2T} \coth \frac{\hbar\omega}{2T}, \quad (2.357)$$

which tends to unity in the classical limit ( $\hbar\omega \ll T$ ). This extra factor is thus the general correspondence between the correlation of classical random forces and the quantum ones.

## 2.13 The Green-Kubo Formula for Heat Conductivity

In this section we shall use the technique introduced in the last two sections to derive the Green-Kubo formulas, especially the formula for heat conductivity which can not be derived from time dependent perturbation theory.

An electric field does mechanical work on the electricity current. The work done per unit time and volume is evidently equal to the scalar product  $-e\mathbf{j} \cdot \mathbf{E}$ , where  $\mathbf{j}$  is the particle number current density and  $e$  is the positive electron charge. If this work dissipates into heat, such process is called *Joule heating*. The evolution of heat results in an increase in the entropy of the body. When an amount of heat  $-e\mathbf{j} \cdot \mathbf{E}d\mathcal{V}$  is evolved in a volume element  $d\mathcal{V}$ , the corresponding entropy increment is  $-(e\mathbf{j} \cdot \mathbf{E}/T)d\mathcal{V}$ . The rate of change of the total entropy of the body is therefore

$$\frac{dS}{dt} = -e \int \frac{\mathbf{j} \cdot \mathbf{E}}{T} d\mathcal{V}. \quad (2.358)$$

The entropy is also changed by the heat current itself. According to the equation of continuity, the heat change in a volume element  $d\mathcal{V}$  due to the heat current is just the gradient of the heat current  $-\nabla(\mathbf{q} - \mu\mathbf{j})d\mathcal{V}$ , where  $\mathbf{q}$  is the energy current and  $\mu$  is the chemical potential. Accordingly,

the entropy change in the volume element is  $-\nabla(\mathbf{q} - \mu\mathbf{j})/T]d\mathcal{V}$  and the rate of change of the total entropy due to heat current is

$$\frac{dS}{dt} = - \int \frac{\nabla \cdot (\mathbf{q} - \mu\mathbf{j})}{T} d\mathcal{V}. \quad (2.359)$$

Integrating this formula by parts and assuming the boundary integral to vanish we obtain that

$$\frac{dS}{dt} = - \int \frac{(\mathbf{q} - \mu\mathbf{j}) \cdot \nabla T}{T^2} d\mathcal{V}. \quad (2.360)$$

Combining (2.358) and (2.360) gives the final expression for the rate of change of the total entropy as [21, 24]

$$\frac{dS}{dt} = - \int \left[ \frac{e\mathbf{j} \cdot \mathbf{E}}{T} + \frac{(\mathbf{q} - \mu\mathbf{j}) \cdot \nabla T}{T^2} \right] d\mathcal{V}. \quad (2.361)$$

According to the general fluctuation theory, the rate of change of entropy can be written like (2.298) in terms of physical quantities  $x_i$  and the corresponding thermodynamic conjugate  $X_i$  as

$$\dot{S} = - \sum_i \dot{x}_i X_i. \quad (2.362)$$

Now we define  $\dot{x}_1(\mathbf{r})$  as the electricity current density  $-e\mathbf{j}(\mathbf{r})$  and  $\dot{x}_2(\mathbf{r})$  as the heat current density  $(\mathbf{q} - \mu\mathbf{j})(\mathbf{r})$ , and their spatial components as

$$\dot{x}_{1a}(\mathbf{r}) = -ej_a(\mathbf{r}), \quad \dot{x}_{2a}(\mathbf{r}) = (q - \mu j)_a(\mathbf{r}), \quad (2.363)$$

where  $a = x, y, z$  is a spatial component index. Replacing the integral (2.361) by a sum over the portions  $\Delta\mathcal{V}$  it is easy to see that the corresponding thermodynamic conjugates  $X_{1a}$  and  $X_{2a}$  are

$$X_{1a}(\mathbf{r}) = -\frac{E_a(\mathbf{r})}{T} \Delta\mathcal{V}, \quad X_{2a}(\mathbf{r}) = \frac{(\nabla T)_a(\mathbf{r})}{T^2} \Delta\mathcal{V}. \quad (2.364)$$

Once  $x_{ia}$  and  $X_{ia}$  are specified, the corresponding kinetic coefficients  $\gamma_{ik,ab}(\mathbf{r}, \mathbf{r}')$  are also specified, here  $i, k = 1, 2$  and  $a, b = x, y, z$ . And the corresponding Langevin equations are

$$\dot{x}_{ia}(\mathbf{r}) = - \sum_{k,b,\mathbf{r}'} \gamma_{ik,ab}(\mathbf{r}, \mathbf{r}') X_{kb}(\mathbf{r}') + y_{ia}(\mathbf{r}), \quad (2.365)$$

where the sum over  $\mathbf{r}'$  means the sum over the corresponding infinitesimal volume portion  $\Delta\mathcal{V}$ . Note that the random forces  $y_{ia}$  can be also viewed as a random flux since  $\dot{x}_{ia}$  are currents here. According to (2.356), we have

$$[y_{ia}(\mathbf{r})y_{kb}(\mathbf{r}')]\omega = [\gamma_{ik,ab}(\mathbf{r}, \mathbf{r}') + \gamma_{ki,ba}(\mathbf{r}', \mathbf{r})]\frac{\hbar\omega}{2T} \coth \frac{\hbar\omega}{2T}. \quad (2.366)$$

Now consider that the transport coefficients, and also the kinetic coefficients, are complex functions of frequency, so we can replace  $\gamma_{ik,ab}(\mathbf{r}, \mathbf{r}') + \gamma_{ki,ba}(\mathbf{r}', \mathbf{r})$  by the real parts of the frequency dependent functions that

$$[y_{ia}(\mathbf{r})y_{kb}(\mathbf{r}')]\omega = \frac{\hbar\omega}{T} \coth \frac{\hbar\omega}{2T} \operatorname{Re} \gamma_{ik,ab}(\omega; \mathbf{r}, \mathbf{r}'). \quad (2.367)$$

The validity of the replacement of  $\gamma_{ik,ab} + \gamma_{ki,ba}$  by their real parts can be seen from the following. If this expression depends on time, then according to the general derivation the explicit form should be  $\gamma_{ik,ab}(\mathbf{r}, \mathbf{r}'; t) + \gamma_{ki,ba}(\mathbf{r}', \mathbf{r}; -t)$ , or collaborating with Onsager's principle  $\gamma_{ik,ab}(\mathbf{r}, \mathbf{r}'; t) + \gamma_{ik,ba}(\mathbf{r}, \mathbf{r}'; -t)$ . After the Fourier transformation the expressions are just  $2 \operatorname{Re} \gamma_{ik,ab}(\omega; \mathbf{r}, \mathbf{r}')$ .

The equation (2.367) may be viewed differently by reading them "from right to left". In other words, write them as

$$\operatorname{Re} \gamma_{ik,ab}(\mathbf{r}, \mathbf{r}'; \omega) = [y_{ia}(\mathbf{r})y_{kb}(\mathbf{r}')]\omega \frac{T}{\hbar\omega} \tanh \frac{\hbar\omega}{2T}. \quad (2.368)$$

In this formula we can replace the random forces  $y_{ia}$  (here we can regard them as random currents) by the currents themselves. The reason can be seen from (2.365): in equilibrium the first term disappears, the fluctuations of currents  $\dot{x}_{ia}$  are the same as the random currents  $y_{ia}$ . In other words, all the fluctuations of currents are represented by the random currents  $y_{ia}$ . Unlike  $y_{ia}$ , the currents  $\dot{x}_{ia}$  themselves have direct mechanical significance and corresponds to a definite quantum-mechanical operator  $\hat{x}_{ia}(\mathbf{r}, t)$  which can be expressed in terms of the operators of dynamic variables of particles in the medium. Therefore we arrive at the formula [42]

$$\begin{aligned} \operatorname{Re} \gamma_{ik,ab}(\omega; \mathbf{r}, \mathbf{r}') &= \frac{T}{\hbar\omega} \tanh \frac{\hbar\omega}{2T} \times \int_0^\infty \frac{1}{2} \langle \hat{x}_{ia}(t, \mathbf{r}) \hat{x}_{kb}(0, \mathbf{r}') + \hat{x}_{kb}(0, \mathbf{r}') \hat{x}_{ia}(t, \mathbf{r}) \rangle e^{i\omega t} dt, \\ &= [\hat{x}_{ia}(\mathbf{r}) \hat{x}_{kb}(\mathbf{r}')]\omega \frac{T}{\hbar\omega} \tanh \frac{\hbar\omega}{2T}. \end{aligned} \quad (2.369)$$



According to the fluctuation-dissipation theorem (2.131) or (2.274), the correlation function can be related to the commutation of the operators by

$$[\hat{x}_{ia}(\mathbf{r})\hat{x}_{kb}(\mathbf{r}')]\omega = \coth \frac{\hbar\omega}{2T} \times \text{Re} \int_0^\infty \langle [\hat{x}_{ia}(t, \mathbf{r}), \hat{x}_{kb}(0, \mathbf{r}')] \rangle e^{i\omega t} dt, \quad (2.370)$$

note here is the real part of the integral, not the imaginary part of the Green's function in (2.274) since in the definition of the Green's function there is an extra factor  $\frac{i}{\hbar}$ .

A comparison between (2.369) and (2.370) immediately gives

$$\text{Re} \gamma_{ik,ab}(\omega; \mathbf{r}, \mathbf{r}') = \frac{T}{\hbar\omega} \times \text{Re} \int_0^\infty \langle [\hat{x}_{ia}(t, \mathbf{r}), \hat{x}_{kb}(0, \mathbf{r}')] \rangle e^{i\omega t} dt. \quad (2.371)$$

The two sides of this formula contain the real parts of functions of  $\omega$  which have no singularity in the upper half-plane of the complex variable  $\omega$ . And because their real parts are equal on the real axis of  $\omega$ , it immediately follows that these functions themselves are equal, and we arrive at the final formula

$$\gamma_{ik,ab}(\omega; \mathbf{r}, \mathbf{r}') = \frac{T}{\hbar\omega} \int_0^\infty \langle [\hat{x}_{ia}(t, \mathbf{r}), \hat{x}_{kb}(0, \mathbf{r}')] \rangle e^{i\omega t} dt. \quad (2.372)$$

However, these kinetic coefficients can not correspond to the usual transport coefficients yet. The reason is that the thermodynamic conjugate  $X_{ia}(\mathbf{r})$  contains an infinitesimal volume portion  $d\mathcal{V}$ , and this situation is similar to when we discussed the difference between conductivity  $\sigma(\omega; \mathbf{r}, \mathbf{r}')$  and the usual electrical conductivity  $\sigma(\omega)$  in section 2.9. Following the same procedure as the derivation in (2.210), we obtain that

$$\gamma_{ik,ab}(\omega) = \frac{1}{\mathcal{V}} \int d^3\mathbf{r} d^3\mathbf{r}' \gamma_{ik,ab}(\omega; \mathbf{r}, \mathbf{r}'), \quad (2.373)$$

or, explicitly,

$$\begin{aligned} \gamma_{ik,ab}(\omega) &= \frac{T}{\hbar\omega} \int \int_0^\infty \langle [\hat{x}_{ia}(t, \mathbf{r}), \hat{x}_{kb}(0, 0)] \rangle e^{i\omega t} dt d^3\mathbf{r} \\ &= \frac{T}{\hbar\omega} \lim_{\mathbf{k} \rightarrow 0} \int \int_0^\infty \langle [\hat{x}_{ia}(t, \mathbf{r}), \hat{x}_{kb}(0, 0)] \rangle e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} dt d^3\mathbf{r}, \end{aligned} \quad (2.374)$$

where  $\mathbf{k} \rightarrow 0$  corresponds to the hydrodynamic approximation.

From the above discussion it is evident that the kinetic coefficients  $\gamma_{ik,ab}$  correspond to the

transport coefficients defined in (2.88). To specific, it is easy to see that

$$\gamma_{11,ab} = \sigma_{ab}T, \quad \gamma_{12,ab} = \gamma_{21,ab} = (\sigma S)_{ab}T^2, \quad \gamma_{22} = k_{ab}T^2, \quad (2.375)$$

where  $\sigma$  is the electrical conductivity,  $S$  is the Seebeck coefficient and  $k$  is the heat conductivity. It should be noted that according to Onsager's principle the indices  $a$  and  $b$  are also symmetric, for instance  $\sigma_{ab} = \sigma_{ba}$ . Thus the formula for electrical conductivity and thermoelectric coefficients are

$$\sigma_{ab}(\omega) = \frac{e^2}{\hbar\omega} \lim_{\mathbf{k} \rightarrow 0} \int \int_0^\infty \langle [\hat{j}_a(t, \mathbf{r}), \hat{j}_b(0, 0)] \rangle e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} dt d^3\mathbf{r}, \quad (2.376)$$

and

$$(\sigma S)_{ab}(\omega) = -\frac{e}{\hbar\omega T} \lim_{\mathbf{k} \rightarrow 0} \int \int_0^\infty \langle [(\hat{q} - \hat{j})_a(t, \mathbf{r}), \hat{j}_b(0, 0)] \rangle e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} dt d^3\mathbf{r}, \quad (2.377)$$

the above two expressions coincide with the Green-Kubo formulas (2.213) and (2.217) discussed in previous sections. And the Green-Kubo formula for heat conductivity is just the formula for  $\gamma_{22,ab}(\omega)$  that

$$k_{ab}(\omega) = \frac{1}{\hbar\omega T} \lim_{\mathbf{k} \rightarrow 0} \int \int_0^\infty \langle [(\hat{q} - \hat{j})_a(t, \mathbf{r}), (\hat{q} - \hat{j})_b(0, 0)] \rangle e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} dt d^3\mathbf{r}. \quad (2.378)$$

With these Green-Kubo formulas, the corresponding Kubo-Greenwood formulas can be also derived by just replacing the corresponding current operator in the Kubo-Greenwood formula discussed in the previous sections.

## Chapter 3

# Dynamical Mean-Field Theory

Dynamical mean-field theory [55, 56] is a method to calculate the electronic structure of strongly correlated systems. This method is non-perturbative and thus in principle can treat the system in any parameter region. The essential idea of the dynamical mean-field theory is to map the original lattice model into an impurity model embedded in an effective medium which is determined self-consistently, and thus reduces a many body problem into a single body problem. The essential difference between the dynamical mean-field theory and the usual Weiss mean-field is that the “mean-field” in the dynamical mean-field is a function, not just a number. Therefore in the dynamical mean-field theory frame all quantum fluctuations of the system are preserved, and this is the reason why it is called “dynamical”. In this chapter we shall give a brief review of the dynamical mean-field theory.

### 3.1 Anderson Impurity Model

The key idea of dynamical mean-field theory is to map a lattice problem into an impurity problem, and such an impurity problem can be represented by Anderson’s impurity model [57]. In this section we shall briefly introduce the single orbit Anderson impurity model. This model was originally proposed by Philip Anderson, and later it was introduced to study the famous Kondo model [13].

The typical Hamiltonian of the Anderson impurity model writes

$$\hat{H} = \sum_{k\sigma} \varepsilon_k \hat{a}_{k\sigma}^\dagger \hat{a}_{k\sigma} - \mu \sum_{\sigma} \hat{c}_{\sigma}^\dagger \hat{c}_{\sigma} + \sum_{k\sigma} V_k (\hat{a}_{k\sigma}^\dagger \hat{c}_{\sigma} + \hat{c}_{\sigma}^\dagger \hat{a}_{k\sigma}) + U \hat{n}_{\uparrow} \hat{n}_{\downarrow}, \quad (3.1)$$

where  $\sigma$  is the spin index and

$$\hat{n}_{\uparrow} = \hat{c}_{\uparrow}^\dagger \hat{c}_{\uparrow}, \quad \hat{n}_{\downarrow} = \hat{c}_{\downarrow}^\dagger \hat{c}_{\downarrow}. \quad (3.2)$$

In this Hamiltonian the operators  $\hat{a}_{k\sigma}^\dagger, \hat{a}_{k\sigma}$  represent an electron band and  $\varepsilon_k$  is the dispersion relation of this electron band. The operators  $\hat{c}_{\sigma}^\dagger$  and  $\hat{c}_{\sigma}$  represent a single site impurity, and this site has a chemical potential  $\mu$  and a Coulomb interaction  $U$  between electrons. The term  $\sum_{k\sigma} V_k (\hat{a}_{k\sigma}^\dagger \hat{c}_{\sigma} + \hat{c}_{\sigma}^\dagger \hat{a}_{k\sigma})$  represent the interchanges of the electrons between the electron band and the impurity, and it is usually called the *hybridization* term.

### Matsubara Green's Function for Anderson Impurity Model

The *Matsubara Green's function*, which is also called *temperature Green's function*, was developed by Takeo Matsubara in 1955 [58]. It is suitable for calculating the thermodynamic properties of the system. An advantage of Matsubara Green's function is that it can be evaluated by Monte Carlo method.

We first define the operators in Matsubara representation as

$$\hat{c}_{\sigma}(\tau) = e^{\tau \hat{H}} \hat{c}_{\sigma} e^{-\tau \hat{H}}, \quad \hat{c}_{\sigma}^{\dagger}(\tau) = e^{\tau \hat{H}} \hat{c}_{\sigma}^{\dagger} e^{-\tau \hat{H}}, \quad (3.3)$$

where  $\tau$  is an auxiliary real variable. These operators formally differ from the operators in Heisenberg representation in that the real time  $t$  in the latter is replaced by the imaginary variable  $-i\hbar\tau$ . Such a replacement is also known as *Wick rotation* [59]. Therefore sometimes we say that the Matsubara operators evolve in imaginary time. It should be emphasized that the operator  $\hat{c}_{\sigma}$  is not the same as the Hermitian conjugate  $[\hat{c}_{\sigma}(\tau)]^{\dagger}$ .

The Matsubara Green's function for the impurity is defined as

$$G_{\sigma\sigma'}(\tau, \tau') = -\langle T_{\tau} \hat{c}_{\sigma}(\tau) \hat{c}_{\sigma'}^{\dagger}(\tau') \rangle, \quad (3.4)$$

where  $T_\tau$  is the “ $\tau$ -chronological operator”, which places operators from right to left in order of increasing  $\tau$  (note that, just like the effect of time ordering operator, for Fermion the sign need to be changed when operators are interchanged). The symbol  $\langle \dots \rangle$  denotes the average over the grand canonical distribution, then the explicit form of the Matsubara Green’s function is

$$G_{\sigma\sigma'}(\tau, \tau') = -\frac{1}{Z} \text{Tr} \left[ e^{-\beta\hat{H}} T_\tau \hat{c}_\sigma(\tau) \hat{c}_{\sigma'}^\dagger(\tau') \right], \quad (3.5)$$

where  $\beta$  is the inverse of temperature  $1/T$  and  $Z = \text{Tr} e^{-\beta\hat{H}}$  is the partition function. From this expression it is easy to see that the Matsubara Green’s function  $G_{\sigma\sigma'}(\tau, \tau')$  depends only on the difference  $\tau - \tau'$ . For example, let  $\tau < \tau'$  then

$$\begin{aligned} G_{\sigma\sigma'}(\tau, \tau') &= \frac{1}{Z} \text{Tr} \left[ e^{-\beta\hat{H}} \hat{c}_{\sigma'}^\dagger(\tau') \hat{c}_\sigma(\tau) \right] \\ &= \frac{1}{Z} \text{Tr} \left[ e^{-\beta\hat{H}} e^{\tau'\hat{H}} \hat{c}_{\sigma'}^\dagger e^{(\tau-\tau')\hat{H}} \hat{c}_\sigma e^{-\tau\hat{H}} \right], \end{aligned} \quad (3.6)$$

or with a cyclic interchange of the factors in the trace,

$$G_{\sigma\sigma'}(\tau, \tau') = \frac{1}{Z} \text{Tr} \left[ e^{-(\beta+\tau-\tau')\hat{H}} \hat{c}_{\sigma'}^\dagger e^{(\tau-\tau')\hat{H}} \hat{c}_\sigma \right], \quad \tau - \tau' < 0. \quad (3.7)$$

Similarly, if  $\tau > \tau'$  then

$$G_{\sigma\sigma'}(\tau, \tau') = -\frac{1}{Z} \text{Tr} \left[ e^{-[\beta-(\tau-\tau')]\hat{H}} \hat{c}_\sigma e^{-(\tau-\tau')\hat{H}} \hat{c}_{\sigma'}^\dagger \right], \quad \tau - \tau' > 0. \quad (3.8)$$

According to the discussion above, we can write the Matsubara Green’s function with only one variable  $\tau$  as

$$G_{\sigma\sigma'}(\tau) = -\langle T_\tau \hat{c}_\sigma(\tau) \hat{c}_{\sigma'}^\dagger \rangle, \quad (3.9)$$

or explicitly

$$G_{\sigma\sigma'}(\tau) = \begin{cases} \frac{1}{Z} \text{Tr} \left[ e^{-(\beta+\tau)\hat{H}} \hat{c}_{\sigma'}^\dagger e^{\tau\hat{H}} \hat{c}_\sigma \right], & \tau < 0; \\ -\frac{1}{Z} \text{Tr} \left[ e^{-(\beta-\tau)\hat{H}} \hat{c}_\sigma e^{-\tau\hat{H}} \hat{c}_{\sigma'}^\dagger \right], & \tau > 0. \end{cases} \quad (3.10)$$

In practice the variable  $\tau$  only takes values in a finite range  $-\beta \leq \tau \leq \beta$  and the values of  $G_{\sigma\sigma'}(\tau)$  for  $-\beta \leq \tau \leq 0$  and  $0 \leq \tau \leq \beta$  are related in a simple manner. When  $\tau > 0$ , with a cyclic

interchange of the factors in the trace,  $G_{\sigma\sigma'}(\tau)$  can be written as

$$G_{\sigma\sigma'}(\tau) = -\frac{1}{Z} \text{Tr} \left[ e^{-\tau \hat{H}} \hat{c}_{\sigma'}^{\dagger} e^{-(\beta-\tau) \hat{H}} \hat{c}_{\sigma} \right], \quad \tau > 0. \quad (3.11)$$

A comparison of the above expression with (3.10) for  $\tau < 0$  immediately gives

$$G_{\sigma\sigma'}(\tau) = -G_{\sigma\sigma'}(\tau + \beta), \quad \tau < 0; \quad (3.12)$$

note that when  $-\beta \leq \tau < 0$  we have  $0 \leq \tau + \beta < \beta$ . This expression indicates that  $G_{\sigma\sigma'}(\tau)$  is anti periodic with a period  $\beta$ .

Let us expand  $G_{\sigma\sigma'}(\tau)$  as a Fourier series in the range  $0 \leq \tau \leq \beta$  as

$$G_{\sigma\sigma'}(\tau) = \frac{1}{\beta} \sum_{n=-\infty}^{\infty} G_{\sigma\sigma'}(i\omega_n) e^{-i\omega_n \tau}, \quad (3.13)$$

where

$$G_{\sigma\sigma'}(i\omega_n) = \int_0^{\beta} G_{\sigma\sigma'}(\tau) e^{i\omega_n \tau} d\tau. \quad (3.14)$$

Since  $G_{\sigma\sigma'}(\tau)$  is anti periodic, we have

$$\omega_n = \frac{(2n+1)\pi}{\beta} \quad (3.15)$$

for  $n = 0, \pm 1, \pm 2, \dots$ . This  $\omega_n$  is also called *Matsubara frequency*.

## The Perturbation Method for Matsubara Green's Function

The Hamiltonian (3.1) can be split into two parts as

$$\hat{H} = \hat{H}_0 + \hat{H}_I, \quad (3.16)$$

where

$$\hat{H}_0 = \sum_{k\sigma} \varepsilon_k \hat{a}_{k\sigma}^{\dagger} \hat{a}_{k\sigma} - \mu \sum_{\sigma} \hat{c}_{\sigma}^{\dagger} \hat{c}_{\sigma} + \sum_{k\sigma} V_k (\hat{a}_{k\sigma}^{\dagger} \hat{c}_{\sigma} + \hat{c}_{\sigma}^{\dagger} \hat{a}_{k\sigma}) \quad (3.17)$$

is treated as the unperturbed Hamiltonian and

$$\hat{H}_I = U\hat{n}_\uparrow\hat{n}_\downarrow \quad (3.18)$$

is the Coulomb interaction term and treated as the perturbation. Now denote Matsubara wave function by

$$\Psi(\tau) = e^{-\tau\hat{H}}\Psi(0), \quad (3.19)$$

and define Matsubara wave function in interaction picture as

$$\Phi(\tau) = e^{\tau\hat{H}_0}\Psi(\tau) = e^{\tau\hat{H}_0}e^{-\tau\hat{H}}\Psi. \quad (3.20)$$

It is clear that the equation of motion for  $\Phi(\tau)$  is

$$\begin{aligned} \frac{d\Phi(\tau)}{d\tau} &= e^{\tau\hat{H}_0}\hat{H}_0e^{-\tau\hat{H}}\Psi - e^{\tau\hat{H}_0}\hat{H}e^{-\tau\hat{H}}\Psi \\ &= -e^{\tau\hat{H}_0}\hat{H}_Ie^{-\tau\hat{H}_0}[e^{\tau\hat{H}_0}e^{-\tau\hat{H}}\Psi] \\ &= -\hat{H}_I^{(0)}(\tau)\Phi(\tau), \end{aligned} \quad (3.21)$$

where

$$\hat{H}_I^{(0)}(\tau) = e^{\tau\hat{H}_0}\hat{H}_Ie^{-\tau\hat{H}_0} \quad (3.22)$$

is the operator  $\hat{H}_I$  in interaction picture. Thus for an infinitesimal interval  $\delta\tau$  we have

$$\begin{aligned} \Phi(\tau + \delta\tau) &= [1 - \delta\tau\hat{H}_I^{(0)}(\tau)]\Phi(\tau) \\ &= \exp[-\delta\tau\hat{H}_I^{(0)}(\tau)]\Phi(\tau), \end{aligned} \quad (3.23)$$

and then the value of  $\Phi(\tau)$  can be expressed in terms of some initial value  $\Phi(\tau_0)$  by

$$\Phi(\tau) = \hat{S}(\tau, \tau_0)\Phi(\tau_0), \quad (3.24)$$

where

$$\hat{S}(\tau, \tau_0) = \prod_{\tau_i=\tau_0}^{\tau} \exp[-\delta\tau\hat{H}_I^{(0)}(\tau_i)]. \quad (3.25)$$

This product is arranged from right to left in orders of increasing  $\tau$ , and it is understood that we take the limit of the product over all the infinitesimal intervals  $\delta\tau$  between  $\tau$  and  $\tau_0$ . The operator  $\hat{S}$  is the scattering matrix in Matsubara representation and it can be written in a symbolic form

$$\hat{S}(\tau, \tau_0) = T_\tau \exp \left[ - \int_{\tau_0}^{\tau} \hat{H}_I^{(0)}(\tau) d\tau \right]. \quad (3.26)$$

It is clear that we have  $\Phi(0) = \Psi(0)$ , therefore

$$\Phi(\tau) = \hat{S}(\tau, 0)\Psi(0), \quad (3.27)$$

and accordingly the transformation rule for operators from interaction Matsubara picture to Matsubara picture are

$$\hat{c}_\sigma(\tau) = \hat{S}^{-1}(\tau, 0)\hat{c}_\sigma^{(0)}(\tau)\hat{S}(\tau, 0), \quad \hat{c}_\sigma^\dagger(\tau) = \hat{S}^{-1}(\tau, 0)\hat{c}_\sigma^{\dagger(0)}(\tau)\hat{S}(\tau, 0), \quad (3.28)$$

where

$$\hat{c}_\sigma^{(0)}(\tau) = e^{\tau\hat{H}_0}\hat{c}_\sigma e^{-\tau\hat{H}_0}, \quad \hat{c}_\sigma^{\dagger(0)}(\tau) = e^{\tau\hat{H}_0}\hat{c}_\sigma^\dagger e^{-\tau\hat{H}_0}. \quad (3.29)$$

Similar to the perturbation theory for the time-ordered Green's function, we finally get

$$\begin{aligned} G_{\sigma\sigma'}(\tau) &= -\langle \hat{S}^{-1}[T_\tau \hat{c}_\sigma^{(0)}(\tau)\hat{c}_{\sigma'}^\dagger, \hat{S}] \rangle \\ &= -\frac{\text{Tr}\{e^{-\beta\hat{H}}\hat{S}^{-1}[T_\tau \hat{c}_\sigma^{(0)}(\tau)\hat{c}_{\sigma'}^\dagger, \hat{S}]\}}{\text{Tr} e^{-\beta\hat{H}}}, \end{aligned} \quad (3.30)$$

where

$$\hat{S} = \hat{S}(\tau, 0). \quad (3.31)$$

According to the definition of  $\Phi(\tau)$  and (3.27), we have

$$\hat{S} = e^{\beta\hat{H}_0}e^{-\beta\hat{H}}, \quad (3.32)$$

or

$$e^{-\beta\hat{H}_0} = e^{-\beta\hat{H}}\hat{S}^{-1} \quad \text{and} \quad e^{-\beta\hat{H}} = e^{-\beta\hat{H}_0}\hat{S}. \quad (3.33)$$



Thus (3.30) can be written as

$$\begin{aligned} G_{\sigma\sigma'}(\tau) &= -\frac{\text{Tr}\{e^{-\beta\hat{H}_0}[T_\tau\hat{c}_\sigma^{(0)}(\tau)\hat{c}_{\sigma'}^\dagger\hat{S}]\}}{\text{Tr}[e^{-\beta\hat{H}_0}\hat{S}]} \\ &= -\frac{1}{\langle\hat{S}\rangle_0}\langle T_\tau\hat{c}_\sigma^{(0)}(\tau)\hat{c}_{\sigma'}^\dagger\hat{S}\rangle_0, \end{aligned} \quad (3.34)$$

where the symbol  $\langle\cdots\rangle_0$  denotes the averaging over the states of the unperturbed system.

The unperturbed Matsubara Green's function is defined as

$$G_{\sigma\sigma'}^{(0)}(\tau) = -\langle T_\tau\hat{c}_\sigma^{(0)}(\tau)\hat{c}_{\sigma'}^\dagger\rangle_0. \quad (3.35)$$

Once the unperturbed Matsubara Green's function is known, we can evaluate the value of Matsubara Green's function via Wick's theorem. Here we shall give the formal expression of the unperturbed Matsubara Green's function in frequency domain for Anderson impurity model without the derivation:

$$G_{\sigma\sigma'}^{(0)}(i\omega_n) = \delta_{\sigma\sigma'} \left[ i\omega_n + \mu - \int_{-\infty}^{\infty} d\omega \frac{\Delta(\omega)}{i\omega_n - \omega} \right]^{-1}, \quad (3.36)$$

where

$$\Delta(\omega) = \sum_k V_k^2 \delta(\omega - \varepsilon_k). \quad (3.37)$$

The above formal expression can be derived using *influence functional* technique developed by Richard Feynman and Frank Vernon [61], and we shall leave the derivation in later sections.

A program is called *impurity solver* if it calculates the Green's function according to the unperturbed Green's function for the impurity model. The impurity solver plays a fundamental role in the dynamical mean-field theory.

## 3.2 The Basic Procedures of the Dynamical Mean-Field Theory

The *Hubbard model* [60] is a typical model of strongly correlated systems, and in this chapter we shall use it to demonstrate the dynamical mean-field theory. And in this section, for simplicity, we shall just give a basic overview of the dynamical mean-field theory without rigorous derivations.

The Hamiltonian for the Hubbard model is

$$\hat{H} = \sum_{ij,\sigma} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} - \mu \hat{N}, \quad (3.38)$$

where  $\sigma$  is the spin index,  $\hat{c}_{i\sigma}^\dagger$  ( $\hat{c}_{i\sigma}$ ) is the creation (annihilation) operator at site  $i$  with spin  $\sigma$ , and

$$\hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma}, \quad \hat{N} = \sum_{i\sigma} \hat{n}_{i\sigma} \quad (3.39)$$

are electron number operators. The parameter  $t_{ij}$  is the hopping matrix,  $U$  is the Coulomb energy between two electrons in the same site and  $\mu$  is the chemical potential. This Hamiltonian is sometimes written as

$$\hat{H} = \sum_{ij,\sigma} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \frac{U}{2} \sum_{i\sigma} \hat{n}_{i\sigma} \hat{n}_{i\bar{\sigma}} - \mu \hat{N}, \quad (3.40)$$

where  $\bar{\sigma}$  means the opposite spin of  $\sigma$ .

Now we choose an arbitrary site and label it as site 0. Since the system is translational invariant, which site is chosen does not matter. Then we can split the Hamiltonian as

$$\hat{H} = \hat{H}_0 + \hat{H}_I, \quad (3.41)$$

where

$$\hat{H}_I = U \hat{n}_{0\uparrow} \hat{n}_{0\downarrow} \quad (3.42)$$

and  $\hat{H}_0$  is split further as

$$\hat{H}_0 = -\mu \sum_{\sigma} \hat{n}_{0\sigma} + \hat{H}_{\text{bath}} + \hat{H}_{\text{hyb}}, \quad (3.43)$$

where

$$\left\{ \begin{array}{l} \hat{H}_{\text{bath}} = -\mu \sum_{i \neq 0} \sum_{\sigma} \hat{n}_{i\sigma} + U \sum_{i \neq 0} \sum_{\sigma} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + \sum_{i,j \neq 0} \sum_{\sigma} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma}; \\ \hat{H}_{\text{hyb}} = \sum_{i \neq 0} \sum_{\sigma} (t_{i0} \hat{c}_{i\sigma}^\dagger \hat{c}_{0\sigma} + t_{0i} \hat{c}_{0\sigma}^\dagger \hat{c}_{i\sigma}). \end{array} \right. \quad (3.44)$$

It is clear that after the split we treat the site 0 as an impurity, and this impurity contains a chemical potential term  $-\mu \sum_{\sigma} \hat{n}_{\sigma}$  and an interaction term  $\hat{H}_I$ . All other sites are treated as a bath and the corresponding Hamiltonian is  $\hat{H}_{\text{bath}}$ . The interaction between the impurity and the

bath is just the hopping between them and it is represented by a hybridization Hamiltonian  $\hat{H}_{\text{hyb}}$ .

Assume that the bath Hamiltonian is already diagonalized, thus  $\hat{H}_{\text{bath}}$  can be formally written as

$$\hat{H}_{\text{bath}} = \sum_{k\sigma} \varepsilon_k \hat{a}_{k\sigma}^\dagger \hat{a}_{k\sigma}, \quad (3.45)$$

where  $\varepsilon_k$  is the eigenenergy of state  $k$ . Note that here we use symbol  $\hat{a}$  instead of  $\hat{c}$  to represent the bath in order to distinguish the bath and the impurity. Since the operators for bath are represented by  $\hat{a}$ , the index 0 for the impurity is no longer needed, thus we can write

$$\hat{H}_0 = -\mu \sum_{\sigma} \hat{n}_{\sigma} + \hat{H}_{\text{bath}} + \hat{H}_{\text{hyb}}, \quad (3.46)$$

where

$$\hat{H}_{\text{hyb}} = \sum_{k\sigma} V_k (\hat{c}_{\sigma}^\dagger \hat{a}_{k\sigma} + \hat{a}_{k\sigma}^\dagger \hat{c}_{\sigma}). \quad (3.47)$$

After all the rewriting, the Hamiltonian becomes

$$\hat{H} = -\mu \sum_{\sigma} \hat{n}_{\sigma} + U \hat{n}_{\uparrow} \hat{n}_{\downarrow} + \sum_{k\sigma} \varepsilon_k \hat{a}_{k\sigma}^\dagger \hat{a}_{k\sigma} + \sum_{k\sigma} V_k (\hat{a}_{k\sigma}^\dagger \hat{c}_{\sigma} + \hat{c}_{\sigma}^\dagger \hat{a}_{k\sigma}), \quad (3.48)$$

and this is just the Hamiltonian of the Anderson impurity model. When there is no magnetic field, the spin up state and spin down state are equivalent, therefore we can focus on the Matsubara Green's function without the spin index

$$G(\tau) = G_{\sigma}(\tau) = -\langle T_{\tau} \hat{c}_{\sigma}(\tau) \hat{c}_{\sigma}^\dagger \rangle. \quad (3.49)$$

According to the discussion of Anderson impurity model in the last section, the unperturbed Green's function in frequency domain can be formally written as

$$G_0(i\omega_n) = \left[ i\omega_n + \mu - \int_{-\infty}^{\infty} d\omega \frac{\Delta(\omega)}{i\omega_n - \omega} \right]^{-1}. \quad (3.50)$$

And as usual, the relation between  $G_0$  and  $G$  is given by the Dyson equation

$$G_0^{-1}(i\omega_n) - G^{-1}(i\omega_n) = \Sigma(i\omega_n), \quad (3.51)$$

here in dynamical mean-field theory the self-energy  $\Sigma(i\omega_n)$  is assumed local, i.e. only frequency dependent. If there exists an impurity solver, then once  $G_0$  is given, the function  $G$  and the self-energy  $\Sigma$  can be calculated by it.

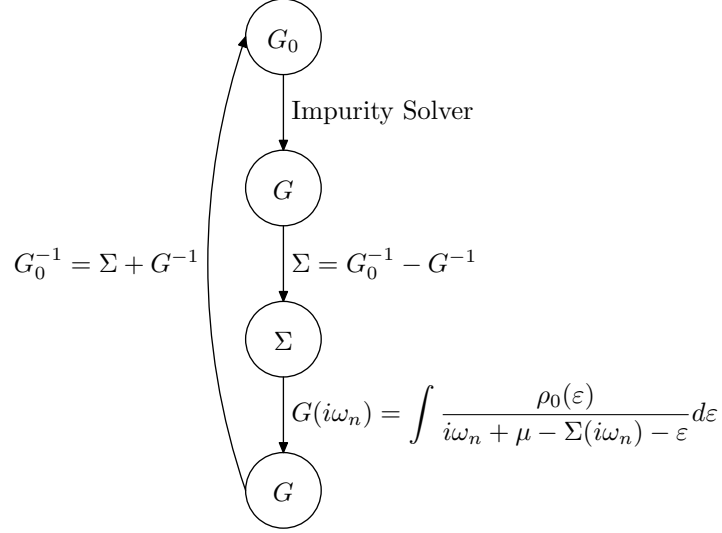


Figure 3.1: Basic dynamical mean-field theory loop.

The function  $G_0$  depends on the properties of the bath, or to be specific, the hybridization term  $\Delta(i\omega_n)$ . Since the impurity site is chosen arbitrarily, the site in the bath is essentially equivalent to the impurity site whose property is determined by  $G$ . And  $G_0$  and  $G$  are related by the Dyson equation (3.51), hence it is possible to get a self-consistent condition for  $G_0$  and  $G$ . Such a condition is given by the formula

$$G(i\omega_n) = \int \frac{\rho_0(\varepsilon)}{i\omega_n + \mu - \varepsilon - \Sigma(i\omega_n)} d\varepsilon, \quad (3.52)$$

where  $\rho_0(\varepsilon)$  is the density of states of the unperturbed system. The derivations of the above formulas is left to later sections and we shall just give a typical dynamical mean-field theory loop here (see Figure 3.1):

1. Choose an unperturbed Matsubara Green's function  $G_0(i\omega_n)$ ;
2. Calculate  $G$  according to given  $G_0$  by impurity solver;
3. Calculate  $\Sigma$  according to the Dyson equation (3.51);
4. Use the self-energy obtained in step 3 to calculate new  $G$  by (3.52) and calculate new  $G_0$  by (3.51);

5. Compare the Green's function in step 2 and step 4, if they are close enough then we can finish loop and a Green's function  $G$  is obtained, otherwise go to step 2 again with  $G_0$  obtained in step 4.

It should be emphasized that to calculate  $G(i\omega_n)$  for a specific  $\omega_n$ , in principle the impurity solver needs the whole unperturbed Green's function  $G_0$ , not only one point of  $G_0$ . In other words, the value  $G(i\omega_n)$  for every specific  $\omega_n$  is a functional of function  $G_0$ . This means that in dynamical mean-field theory, the Green's function, which is a function, acts as the “mean-field”, while in usual Weiss mean-field the “mean-field” is just a number. This is the reason why dynamical mean-field theory contains much more information than Weiss mean-field theory.

And we should also note that the main approximation in dynamical mean-field theory is that the self-energy is local. This approximation let us neglect the spatial fluctuations of the system and makes it possible to map the original problem into an impurity problem.

### 3.3 The Dynamical Mean-Field Theory with Constant Filling

Although the Hubbard model can explain basic features of a strongly correlated electronic system, it is not enough to describe the features of real materials. It is clear that realistic theories must take the explicit electronic and lattice structure into account, and this is usually done by putting the density of states calculated by *first principle calculations* [62] as the unperturbed density of states  $\rho_0$ . First principle calculations are usually done by employing *density functional theory* [63, 64], and the method combining first principle calculations and dynamical mean-field theory [65] is usually denoted by DFT+DMFT.

The density of states calculated by density functional theory can be used directly in dynamical mean-field theory. However, we must be careful about the chemical potential, otherwise it may cause some problems. Here is an example. Let us consider an ideal situation: a half-filling *Bethe lattice* [66, 67], whose electronic density of states is just a semicircle. And we assume the bandwidth is 4, see Figure 3.2(a).

It is clear that the half-filling condition for the Bethe lattice without Coulomb interaction is that  $\mu = 0$ , i.e., the chemical potential is at the band center. However, if Coulomb interaction is turned on then  $\mu = 0$  is not the half-filling condition anymore. This can be seen from Figure 3.2(b):

when  $\mu = 0$  the filling is far less than half. In fact, for Bethe lattice with Coulomb interaction,  $\mu = U/2$  is the half-filling condition. This can be argued as follows.

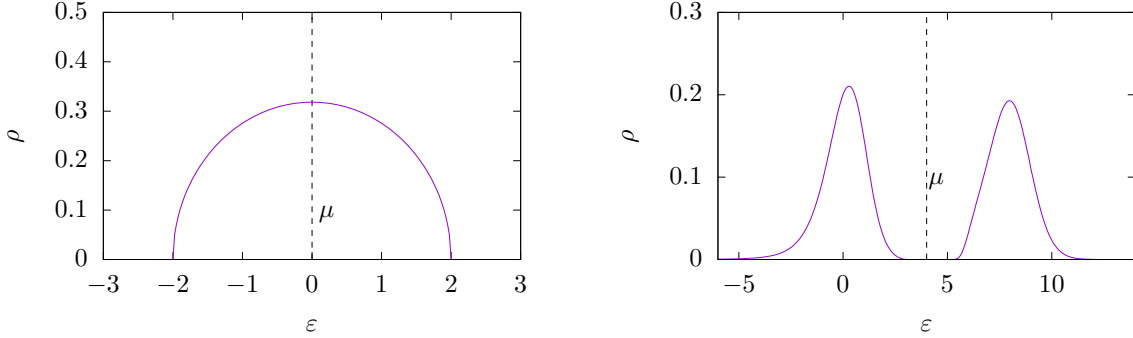
The Hamiltonian of the Hubbard model is written as

$$\hat{H} = -t \sum_{\langle ij \rangle} \sum_{\sigma} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} - \mu \sum_{i\sigma} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{i\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}. \quad (3.53)$$

Here let us apply a particle-hole transformation on this Hamiltonian: replace  $\hat{c}_i$  by  $(-1)^i \hat{c}_i^{\dagger}$  and  $\hat{c}_i^{\dagger}$  by  $(-1)^i \hat{c}_i$ , then the Hamiltonian becomes

$$\hat{H} = -t \sum_{\langle ij \rangle} \sum_{\sigma} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} + \left[ (U - 2\mu) - (U - \mu) \sum_{i\sigma} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{i\sigma} \right] + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}. \quad (3.54)$$

It is easy to see that when  $\mu = U/2$  the term in bracket yields  $-\mu \hat{N}$ , then (3.54) becomes identical with (3.53). In this case we say the system has *particle-hole symmetry*, in other words, the system is half filled.



(a) The density of states of Bethe lattice without Coulomb interaction. The chemical potential is at the middle of the band, which means the half-filling.

(b) The density of states after the dynamical mean-field theory calculation. The value of Coulomb interaction strength  $U$  used here is 8, thus the value of chemical potential should be  $U/2 = 4$  to satisfy the half-filling condition. This form of density of states is extracted from Matsubara Green's function by *maximum entropy* method. The maximum entropy method is employed by  $\Omega$ MaxEnt toolkit [70].

Figure 3.2: The density of states before and after the dynamical mean-field theory calculation.

Therefore when investigating real materials the filling, rather than chemical potential, given by density functional theory should be used for dynamical mean-field theory. It should be noted that in

principle the Coulomb interaction would also affect the electron filling, thus the full DFT+DMFT algorithm [68, 69] should take this into consideration. However, most DFT+DMFT calculations perform a simplified scheme which neglects the change of electron filling caused by Coulomb interaction, i.e., uses a constant electron filling. Such a simplified scheme is usually called “one-shot” dynamical mean-field theory calculation, and it works well if we only want the electronic structure [68].

To perform this one-shot calculation, the chemical potential needs to be adjusted in dynamical mean-field theory loops. Once the Matsubara Green’s function  $G(i\omega_n)$  is obtained, we need to calculate the filling and then update the chemical potential to get the target filling. Since we change only one parameter (chemical potential) in this process, a one dimensional root finder can be used. The recommended finder would be Brent’s false-position plus inverse quadratic substitution root-finder [71], which approaches the speed and accuracy of Newton’s method with the safety of a false-position algorithm, and no need of calculating the derivative of the filling with respect to chemical potential. Figure 3.3 shows a flow diagram for such a loop.

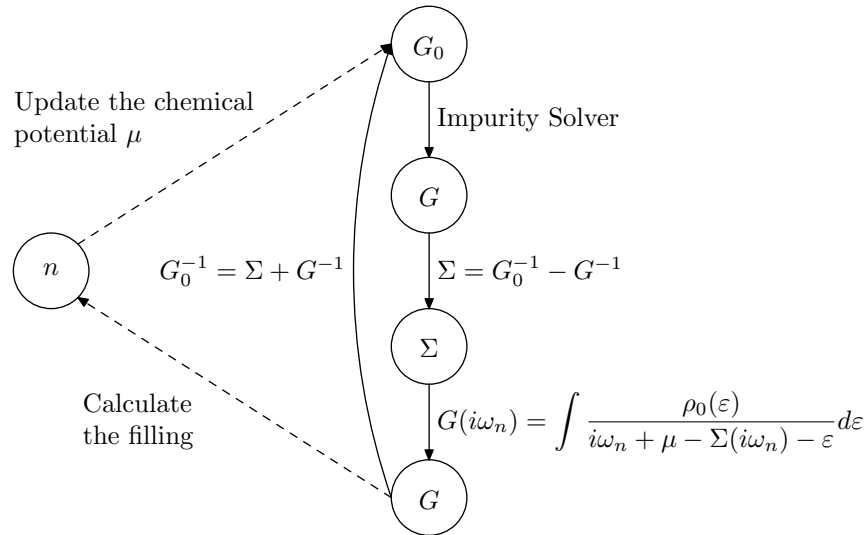


Figure 3.3: The loop for dynamical mean-field theory with constant filling.

### 3.4 Boson Coherent States

The rigorous formalism of dynamical mean-field theory is based on the functional integral formalism. We need to introduce the concept of coherent state in order to develop the functional integral

formalism for a many-body system. The details of the functional integral formalism can be found in Ref [72]. In this section we shall introduce coherent states for a bosonic system.

Let  $\hat{a}_\alpha$  be a bosonic annihilation operator for arbitrary state  $\alpha$ , then the corresponding coherent state  $|\phi\rangle$  is defined as the eigenstate of the annihilation operator:

$$\hat{a}_\alpha |\phi\rangle = \phi_\alpha |\phi\rangle. \quad (3.55)$$

For bosons, such a coherent state can be expanded by vectors in Fock space. To show this, we write the coherent state  $|\phi\rangle$  for  $\hat{a}_\alpha$  as

$$|\phi\rangle = \sum_{n_1, n_2, \dots, n_p, \dots} \phi_{n_1, n_2, \dots, n_p, \dots} |n_1, n_2, \dots, n_p, \dots\rangle, \quad (3.56)$$

where as usual  $|n_1, n_2, \dots, n_p, \dots\rangle$  denotes a normalized state with  $n_1$  particles in state 1,  $n_2$  particles in state 2, and so on. Then an annihilation operator  $\hat{a}_\alpha$  acting on  $|\phi\rangle$  gives

$$\hat{a}_\alpha |\phi\rangle = \phi_\alpha |\phi\rangle = \sum_{n_1, n_2, \dots, n_\alpha, \dots} \sqrt{n_\alpha} \phi_{n_1, n_2, \dots, n_\alpha, \dots} |n_1, \dots, n_\alpha - 1, \dots\rangle, \quad (3.57)$$

which means

$$\phi_\alpha \phi_{n_1, n_2, \dots, n_\alpha - 1, \dots} = \sqrt{n_\alpha} \phi_{n_1, n_2, \dots, n_\alpha, \dots} \quad (3.58)$$

We set the coefficient for vacuum equal to 1, then according to the above formula we obtain

$$\phi_{n_1, n_2, \dots, n_p, \dots} = \frac{\phi_1^{n_1}}{\sqrt{n_1!}} \frac{\phi_2^{n_2}}{\sqrt{n_2!}} \dots \frac{\phi_p^{n_p}}{\sqrt{n_p!}} \dots \quad (3.59)$$

Recalling that

$$|n_1, n_2, \dots, n_p, \dots\rangle = \frac{(\hat{a}_1^\dagger)^{n_1}}{\sqrt{n_1!}} \frac{(\hat{a}_2^\dagger)^{n_2}}{\sqrt{n_2!}} \dots \frac{(\hat{a}_p^\dagger)^{n_p}}{\sqrt{n_p!}} \dots |0\rangle, \quad (3.60)$$

and substituting (3.59) into (3.56) we finally get

$$\begin{aligned} |\phi\rangle &= \sum_{n_1, n_2, \dots, n_p, \dots} \frac{(\phi_1 \hat{a}_1^\dagger)^{n_1}}{n_1!} \frac{(\phi_2 \hat{a}_2^\dagger)^{n_2}}{n_2!} \dots \frac{(\phi_p \hat{a}_p^\dagger)^{n_p}}{n_p!} \dots |0\rangle \\ &= e^{\sum_\alpha \phi_\alpha \hat{a}_\alpha^\dagger} |0\rangle, \end{aligned} \quad (3.61)$$



and correspondingly

$$\langle \phi | = \langle 0 | e^{\sum_{\alpha} \phi_{\alpha}^* \hat{a}_{\alpha}}. \quad (3.62)$$

It is clear that we have

$$\langle \phi | \hat{a}_{\alpha}^{\dagger} = \langle \phi | \phi_{\alpha}^*. \quad (3.63)$$

The overlap of two coherent states is given by

$$\langle \phi | \phi' \rangle = \sum_{n_1, \dots, n_p, \dots} \sum_{n'_1, \dots, n'_p, \dots} \frac{\phi_1^{*n_1}}{\sqrt{n_1!}} \cdots \frac{\phi_p^{*n_p}}{\sqrt{n_p!}} \cdots \frac{\phi'_1{}^{n'_1}}{\sqrt{n'_1!}} \cdots \frac{\phi'_p{}^{n'_p}}{\sqrt{n'_p!}} \cdots \langle n_1, \dots, n_p, \dots | n'_1, \dots, n'_p, \dots \rangle. \quad (3.64)$$

Since the basis  $|n\rangle$  is orthonormal, the scalar product  $\langle n_1, \dots, n_p, \dots | n'_1, \dots, n'_p, \dots \rangle$  is just  $\delta_{n_1 n'_1} \cdots \delta_{n_p n'_p} \cdots$ , which leads to

$$\langle \phi | \phi' \rangle = e^{\sum_{\alpha} \phi_{\alpha}^* \phi_{\alpha}}. \quad (3.65)$$

A crucial property of the coherent states is that they are complete in the Fock space, in other words any vector in Fock space can be expanded in terms of coherent states. This can be expressed by the closure relation

$$\int \left( \prod_{\alpha} \frac{d\phi_{\alpha}^* d\phi_{\alpha}}{2\pi i} \right) e^{-\sum_{\alpha} \phi_{\alpha}^* \phi_{\alpha}} |\phi\rangle \langle \phi| = 1, \quad (3.66)$$

where 1 is the unit operator in Fock space, and the measure is given by

$$\frac{d\phi_{\alpha}^* d\phi_{\alpha}}{2\pi i} = \frac{d(\operatorname{Re} \phi_{\alpha}) d(\operatorname{Im} \phi_{\alpha})}{\pi}. \quad (3.67)$$

To prove (3.66), we first consider one single-particle state and let  $|n\rangle$  denote the state with  $n$  particles in this state, then the integral in (3.66) can be written as

$$\int \frac{d(\operatorname{Re} \phi) d(\operatorname{Im} \phi)}{\pi} e^{-\phi^* \phi} |\phi\rangle \langle \phi| = \int \frac{d(\operatorname{Re} \phi) d(\operatorname{Im} \phi)}{\pi} e^{-\phi^* \phi} \sum_{mn} \frac{\phi^m}{\sqrt{m!}} |m\rangle \frac{\phi^{*n}}{\sqrt{n!}} \langle n|. \quad (3.68)$$

Writing  $\phi$  in polar form  $\phi = \rho e^{i\theta}$  the above integral becomes

$$\begin{aligned} \int \rho \frac{d\rho d\theta}{\pi} e^{-\rho^2} \sum_{mn} \frac{(\rho e^{i\theta})^m}{\sqrt{m!}} \frac{(\rho e^{-i\theta})^n}{\sqrt{n!}} |m\rangle \langle n| &= 2 \int d\rho e^{-\rho^2} \sum_n \frac{\rho^{2n+1}}{n!} |n\rangle \langle n| \\ &= \sum_n \int_0^{\infty} d(\rho^2) e^{-\rho^2} \frac{\rho^{2n}}{n!} |n\rangle \langle n|. \end{aligned} \quad (3.69)$$

Substituting the variable  $x = \rho^2$  into the above expression we obtain

$$\sum_n \int_0^\infty dx x^n e^{-x} \frac{1}{n!} |n\rangle \langle n| = \sum_n \frac{\Gamma(n+1)}{n!} |n\rangle \langle n| = \sum_n |n\rangle \langle n|, \quad (3.70)$$

where  $\Gamma(n)$  is the Gamma function and when  $n$  is a positive integer we have  $\Gamma(n+1) = n!$ . Now generalize to a set of single-particle states  $|n_1, \dots, n_p, \dots\rangle$ , then the integral in (3.66) can be similarly written as

$$\int \left( \prod_\alpha \frac{d\phi_\alpha^* d\phi_\alpha}{2\pi i} \right) e^{-\sum_\alpha \phi_\alpha^* \phi_\alpha} |\phi\rangle \langle \phi| = \sum_{n_1, \dots, n_p, \dots} |n_1, \dots, n_p, \dots\rangle \langle n_1, \dots, n_p, \dots| = 1. \quad (3.71)$$

Thus (3.66) is proved.

This completeness relation allows us to write the trace of an operator in terms of coherent states. Let  $\hat{A}$  be any operator and let  $|n\rangle$  denote a complete set of states. Then

$$\begin{aligned} \text{Tr } \hat{A} &= \sum_n \langle n | \hat{A} | n \rangle \\ &= \int \left( \prod_\alpha \frac{d\phi_\alpha^* d\phi_\alpha}{2\pi i} \right) e^{-\sum_\alpha \phi_\alpha^* \phi_\alpha} \sum_n \langle n | \phi \rangle \langle \phi | \hat{A} | n \rangle \\ &= \int \left( \prod_\alpha \frac{d\phi_\alpha^* d\phi_\alpha}{2\pi i} \right) e^{-\sum_\alpha \phi_\alpha^* \phi_\alpha} \langle \phi | \hat{A} \sum_n | n \rangle \langle n | \phi \rangle \\ &= \int \left( \prod_\alpha \frac{d\phi_\alpha^* d\phi_\alpha}{2\pi i} \right) e^{-\sum_\alpha \phi_\alpha^* \phi_\alpha} \langle \phi | \hat{A} | \phi \rangle. \end{aligned} \quad (3.72)$$

### 3.5 Fermion Coherent States

Now let  $|\phi\rangle$  be a coherent state of fermions, then according to the definition of coherent state we should have

$$\hat{a}_\alpha |\phi\rangle = \phi_\alpha |\phi\rangle, \quad \hat{a}_\beta |\phi\rangle = \phi_\beta |\phi\rangle. \quad (3.73)$$

Since  $\hat{a}_\alpha$  and  $\hat{a}_\beta$  are fermionic operators, the commutation rule shows that

$$\hat{a}_\alpha \hat{a}_\beta = -\hat{a}_\beta \hat{a}_\alpha, \quad (3.74)$$

which means that

$$\phi_\alpha \phi_\beta = -\phi_\beta \phi_\alpha. \quad (3.75)$$

This relation holds for any  $\alpha$  and  $\beta$ , and thus forces all  $\phi_\alpha = 0$  if  $\phi_\alpha$  is an ordinary scalar. Hence the coherent states for fermion can not be expanded in a basis of Fock space directly and we must enlarge the space. The required enlargement can be done by introducing the concept of Grassmann algebra.

### Grassmann Algebra

A Grassmann algebra is defined by a set of generators, which are also called *Grassmann numbers*. It is named after Hermann Grassmann. We denote this set of Grassmann numbers by  $\xi_1, \xi_2, \dots, \xi_n$ . The Grassmann numbers are defined anti-commutative to each other:

$$\xi_\alpha \xi_\beta + \xi_\beta \xi_\alpha = 0, \quad (3.76)$$

and in particular we have

$$\xi_\alpha^2 = 0. \quad (3.77)$$

We also define conjugation in a Grassmann algebra as

$$(\xi_\alpha)^* = \xi_\alpha^*, \quad (\xi_\alpha^*)^* = \xi_\alpha, \quad (3.78)$$

where  $\xi_\alpha^*$  is another Grassmann number associated as the conjugate of  $\xi_\alpha$ . If  $\lambda$  is an ordinary scalar, then

$$(\lambda \xi_\alpha)^* = \lambda^* \xi_\alpha^* \quad (3.79)$$

and for any product of Grassmann numbers

$$(\xi_1 \cdots \xi_n)^* = \xi_n^* \xi_{n-1}^* \cdots \xi_1^*. \quad (3.80)$$

As for ordinary scalar functions, we can define a derivative for Grassmann variable functions. It is defined to be identical to the usual derivative that

$$\frac{\partial}{\partial \xi_\alpha} \xi_\beta = \delta_{\alpha\beta}. \quad (3.81)$$

However, there is a crucial difference between Grassmann derivative and usual derivative that the derivative operator  $\partial/\partial\xi_\alpha$  must be adjacent to  $\xi_\alpha$ , if not then the position of variable  $\xi_\alpha$  need to be swapped. For example,

$$\frac{\partial}{\partial\xi_\alpha}(\xi_\beta\xi_\alpha) = -\frac{\partial}{\partial\xi_\alpha}(\xi_\alpha\xi_\beta) = -\xi_\beta, \quad (3.82)$$

and

$$\frac{\partial}{\partial\xi_\alpha}(\xi_\alpha^*\xi_\alpha) = -\frac{\partial}{\partial\xi_\alpha}(\xi_\alpha\xi_\alpha^*) = -\xi_\alpha^*. \quad (3.83)$$

We can also define an integral on Grassmann algebra as

$$\int d\xi 1 = 0, \quad \int d\xi \xi = 1, \quad (3.84)$$

and for conjugate variables we define

$$\int d\xi^* 1 = 0, \quad \int d\xi^* \xi^* = 1. \quad (3.85)$$

Note that the integral of this form  $\int d\xi^* \xi$  is meaningless, and except this the integral thus defined is identical to the derivative.

Lastly we require the Grassmann numbers to satisfy the following rules with operators that

$$\tilde{\xi}\tilde{a} + \tilde{a}\tilde{\xi} = 0, \quad (3.86)$$

and

$$(\tilde{\xi}\tilde{a})^\dagger = \tilde{a}^\dagger\tilde{\xi}^*, \quad (3.87)$$

where  $\tilde{\xi}$  denotes any Grassmann variable in  $\{\xi_\alpha, \xi_\alpha^*\}$  and  $\tilde{a}$  is any operator in  $\{\hat{a}_\alpha, \hat{a}_\alpha^\dagger\}$ .

### Fermion Coherent States

With the aid of Grassmann numbers, we can define fermion coherent states as

$$\begin{aligned} |\xi\rangle &= e^{-\sum_\alpha \xi_\alpha \hat{a}_\alpha^\dagger} |0\rangle \\ &= \prod_\alpha (1 - \xi_\alpha \hat{a}_\alpha^\dagger) |0\rangle, \end{aligned} \quad (3.88)$$

here we have expanded the exponential function and used the anti-commutative rules of Grassmann numbers.

We now verify that the coherent states thus defined are eigenstates of annihilation operators. It is easy to see that for a single state, the anti-commutation rules of  $\hat{a}$ ,  $\hat{a}^\dagger$  and  $\xi$  gives

$$\hat{a}(1 - \xi\hat{a}^\dagger) |0\rangle = \xi |0\rangle = \xi(1 - \xi\hat{a}^\dagger) |0\rangle. \quad (3.89)$$

And for multiple states noticing the fact that  $\hat{a}_\alpha$  and  $\xi_\alpha$  both commute with the combination  $\xi_\beta\hat{a}_\beta^\dagger$  for  $\beta \neq \alpha$ , we obtain that

$$\begin{aligned} \hat{a}_\alpha |\xi\rangle &= \hat{a}_\alpha \prod_{\beta} (1 - \xi_\beta\hat{a}_\beta^\dagger) |0\rangle \\ &= \prod_{\beta \neq \alpha} (1 - \xi_\beta\hat{a}_\beta) \hat{a}_\alpha (1 - \xi_\alpha\hat{a}_\alpha^\dagger) |0\rangle \\ &= \prod_{\beta \neq \alpha} (1 - \xi_\beta\hat{a}_\beta) \xi_\alpha (1 - \xi_\alpha\hat{a}_\alpha^\dagger) |0\rangle \\ &= \xi_\alpha \prod_{\beta} (1 - \xi_\beta\hat{a}_\beta) |0\rangle \\ &= \xi_\alpha |\xi\rangle. \end{aligned} \quad (3.90)$$

Similarly, the conjugate of the coherent states is defined as

$$\langle \xi | = \langle 0 | e^{-\sum_{\alpha} \hat{a}_{\alpha} \xi_{\alpha}^*} = \langle 0 | e^{\sum_{\alpha} \xi_{\alpha}^* \hat{a}_{\alpha}}, \quad (3.91)$$

and it is a left eigenstate of  $\hat{a}_\alpha^\dagger$ :

$$\langle \xi | \hat{a}_\alpha^\dagger = \langle \xi | \xi_\alpha^*. \quad (3.92)$$

The overlap of two coherent states is easily calculated:

$$\begin{aligned} \langle \xi | \xi' \rangle &= \langle 0 | \prod_{\alpha} (1 + \xi_{\alpha}^* \hat{a}_{\alpha}) \prod_{\beta} (1 - \xi'_{\beta} \hat{a}_{\beta}^\dagger) |0\rangle \\ &= \langle 0 | \prod_{\alpha} (1 + \xi_{\alpha}^* \hat{a}_{\alpha}) (1 - \xi'_{\alpha} \hat{a}_{\alpha}) |0\rangle \\ &= \prod_{\alpha} (1 + \xi_{\alpha}^* \xi'_{\alpha}) \\ &= e^{\sum_{\alpha} \xi_{\alpha}^* \xi'_{\alpha}}. \end{aligned} \quad (3.93)$$

As in the Boson case, there is also a closure relation which may be written as

$$\int \left( \prod_{\alpha} d\xi_{\alpha}^* d\xi_{\alpha} \right) e^{-\sum_{\alpha} \xi_{\alpha}^* \xi_{\alpha}} |\xi\rangle \langle \xi| = 1, \quad (3.94)$$

where 1 denotes the unit operator in the Fermion Fock space. To prove this closure relation, we denote the left side of the above expression by operator  $\hat{A}$  that

$$\hat{A} = \int \left( \prod_{\alpha} d\xi_{\alpha}^* d\xi_{\alpha} \right) e^{-\sum_{\alpha} \xi_{\alpha}^* \xi_{\alpha}} |\xi\rangle \langle \xi|. \quad (3.95)$$

To prove (3.94), it is sufficient to prove that for any vectors of the basis of the Fock space we have

$$\langle \alpha_1 \cdots \alpha_n | \hat{A} | \beta_1 \cdots \beta_m \rangle = \langle \alpha_1 \cdots \alpha_n | \beta_1 \cdots \beta_m \rangle. \quad (3.96)$$

Since the coherent states are eigenstates of annihilation operators we have

$$\begin{aligned} \langle \alpha_1 \cdots \alpha_n | \xi \rangle &= \langle 0 | \hat{a}_{\alpha_n} \cdots \hat{a}_{\alpha_1} | \xi \rangle \\ &= \xi_{\alpha_n} \cdots \xi_{\alpha_1}, \end{aligned} \quad (3.97)$$

and similarly for its conjugate equation:

$$\begin{aligned} \langle \xi | \beta_1 \cdots \beta_m \rangle &= \langle \xi | \hat{a}_{\beta_1}^{\dagger} \cdots \hat{a}_{\beta_m}^{\dagger} | 0 \rangle \\ &= \xi_{\beta_1}^* \cdots \xi_{\beta_m}^*, \end{aligned} \quad (3.98)$$

note that here we have use the property that

$$\langle \xi | 0 \rangle = \langle 0 | \xi \rangle = 1. \quad (3.99)$$

Therefore we obtain that

$$\begin{aligned} \langle \alpha_1 \cdots \alpha_n | \hat{A} | \beta_1 \cdots \beta_m \rangle &= \int \left( \prod_{\alpha} d\xi_{\alpha}^* d\xi_{\alpha} \right) e^{-\sum_{\alpha} \xi_{\alpha}^* \xi_{\alpha}} \langle \alpha_1 \cdots \alpha_n | \xi \rangle \langle \xi | \beta_1 \cdots \beta_m \rangle \\ &= \int \left( \prod_{\alpha} d\xi_{\alpha}^* d\xi_{\alpha} \right) \prod_{\alpha} (1 - \xi_{\alpha}^* \xi_{\alpha}) \xi_{\alpha_n} \cdots \xi_{\alpha_1} \xi_{\beta_1}^* \cdots \xi_{\beta_m}^*. \end{aligned} \quad (3.100)$$

Now consider the integrals which may be used in (3.100) for a particular state  $\gamma$ :

$$\int d\xi_\gamma^* d\xi_\gamma (1 - \xi_\gamma^* \xi_\gamma) \begin{Bmatrix} \xi_\gamma \xi_\gamma^* \\ \xi_\gamma^* \\ \xi_\gamma \\ 1 \end{Bmatrix} = \begin{Bmatrix} 1 \\ 0 \\ 0 \\ 1 \end{Bmatrix}. \quad (3.101)$$

Thus the integral in (3.100) is non-vanishing only if each state  $\gamma$  is either occupied in both  $\langle \alpha_1 \cdots \alpha_n |$  and  $|\beta_1 \cdots \beta_m\rangle$  or unoccupied in both states, which requires  $m = n$  and  $\{\alpha_1 \cdots \alpha_n\}$  must be some permutation of  $\{\beta_1 \cdots \beta_n\}$ . And the order of the permutation is the same in (3.96), hence (3.96) is proved.

This closure relation allows us to write the trace of an operator in terms of coherent states. First, notice that if  $|\alpha\rangle, |\beta\rangle$  are two vectors in Fock space and  $|\xi\rangle$  is a coherent state, then in the integral

$$\langle \alpha | \xi \rangle \langle \xi | \beta \rangle = \langle -\xi | \beta \rangle \langle \alpha | \xi \rangle. \quad (3.102)$$

This can be seen from (3.97) and (3.98) that

$$\begin{aligned} \langle \alpha | \xi \rangle \langle \xi | \beta \rangle &= \xi_{\alpha_n} \cdots \xi_{\alpha_1} \xi_{\beta_1}^* \cdots \xi_{\beta_n}^* \\ &= (-\xi_{\beta_1}^*) \cdots (-\xi_{\beta_n}^*) \xi_{\alpha_n} \cdots \xi_{\alpha_1} \\ &= \langle -\xi | \beta \rangle \langle \alpha | \xi \rangle, \end{aligned} \quad (3.103)$$

note that  $2n - 1$  interchanges are needed when we move the right most side term to left most side and these interchanges yield an extra factor  $(-1)^{2n-1} = -1$ .

Now let  $\{|n\rangle\}$  be a complete set of states in Fock space, then the trace of an operator  $\hat{A}$  can be written as

$$\begin{aligned} \text{Tr } \hat{A} &= \sum_n \langle n | \hat{A} | n \rangle \\ &= \int \left( \prod_\alpha d\xi_\alpha^* d\xi_\alpha \right) e^{-\sum_\alpha \xi_\alpha^* \xi_\alpha} \sum_n \langle n | \xi \rangle \langle \xi | \hat{A} | n \rangle \\ &= \int \left( \prod_\alpha d\xi_\alpha^* d\xi_\alpha \right) e^{-\sum_\alpha \xi_\alpha^* \xi_\alpha} \langle -\xi | \hat{A} \sum_n | n \rangle \langle n | \xi \rangle \\ &= \int \left( \prod_\alpha d\xi_\alpha^* d\xi_\alpha \right) e^{-\sum_\alpha \xi_\alpha^* \xi_\alpha} \langle -\xi | \hat{A} | \xi \rangle. \end{aligned} \quad (3.104)$$

### 3.6 Gaussian Integrals for Coherent States

According to the discussions in the last two sections, the trace of an operator can be expressed in terms of coherent states in an integral form. Looking at (3.72) and (3.104), we shall find that such integrals are in a form of Gaussian integrals. It is indeed possible to develop a Gaussian integral formalism for Grassmann numbers and thus the trace of coherent states can be treated as Gaussian integrals of coherent states.

Let us begin by proving an identity for multidimensional Gaussian integrals over real variables:

$$\int \frac{dx_1 \cdots dx_n}{(2\pi)^{\frac{n}{2}}} e^{-\frac{1}{2}x_i A_{ij} x_j + x_i J_i} = [\det A]^{-\frac{1}{2}} e^{\frac{1}{2}J_i A_{ij}^{-1} J_j}, \quad (3.105)$$

where  $A$  is a real symmetric positive definite matrix and the repeated indices is understood summation over these indices. This identity can be proved by following steps: let  $y_i = x_i - A_{ij}^{-1} J_j$  and  $z_k = O_{ki}^{-1} x_i$ , where  $O$  is the orthogonal transformation which diagonalize  $A$ , we obtain

$$\begin{aligned} \int dx_1 \cdots dx_n e^{-\frac{1}{2}x_i A_{ij} x_j + x_i J_i} &= \int dy_1 \cdots dy_n e^{-\frac{1}{2}y_i A_{ij} y_j} \\ &= \int dz_1 \cdots dz_n e^{-\frac{1}{2} \sum_m a_m z_m^2} \\ &= \prod_{m=1}^n \sqrt{\frac{2\pi}{a_m}} \\ &= \frac{(2\pi)^{\frac{n}{2}}}{[\det A]^{\frac{1}{2}}} e^{\frac{1}{2}J_i A_{ij}^{-1} J_j}. \end{aligned} \quad (3.106)$$

Thus the identity is proved. Note that the requirement that  $A$  is positive definite is to ensure the convergence of the Gaussian integral. A Similar identity for complex variables is

$$\int \left( \prod_{i=1}^n \frac{dx_i^* dx_i}{2\pi i} \right) e^{-x_i^* H_{ij} x_j + J_i^* x_i + J_i x_i^*} = [\det H]^{-1} e^{J_i^* H_{ij}^{-1} J_j}, \quad (3.107)$$

which is valid for a positive definite Hermitian matrix  $H$ . The proof for complex variables is similar to the proof for real variables so we shall skim the derivations, just note that the measure

$$\frac{dx^* dx}{2\pi i} = \frac{d(\operatorname{Re} x) d(\operatorname{Im} x)}{\pi}. \quad (3.108)$$



Finally, we shall prove the analogous identity for Grassmann variables that

$$\int \left( \prod_{i=1}^n d\eta_i^* d\eta_i \right) e^{-\eta_i^* H_{ij} \eta_j + \zeta_i^* \eta_i + \eta_i^* \zeta_i} = [\det H] e^{\zeta_i^* H_{ij}^{-1} \zeta_j}, \quad (3.109)$$

where  $H$  is a Hermitian but not necessarily positive definite matrix and  $\{\zeta_i^*, \zeta_i, \eta_i^*, \eta_i\}$  are Grassmann numbers. To prove this identity, we need to derive the transformation law for an integral under a change of variables for Grassmann variables.

Let us consider an multidimensional integral over Grassmann variables

$$\int d\zeta_1^* d\zeta_1 \cdots d\zeta_n^* d\zeta_n P(\zeta^*, \zeta), \quad (3.110)$$

where  $P(\zeta^*, \zeta)$  is a function of  $\{\zeta_i^*, \zeta_i\}$ . Relabel the variables as

$$(\zeta_1^* \zeta_2^* \cdots \zeta_n^* \zeta_n \zeta_{n-1} \cdots \zeta_1) \equiv (\tilde{\zeta}_1 \tilde{\zeta}_2 \cdots \tilde{\zeta}_{2n}), \quad (3.111)$$

and introduce a new set of variables  $\{\eta_i^*, \eta_i\}$  and relabel them as

$$(\eta_1^* \eta_1 \eta_2^* \eta_2 \cdots \eta_n^* \eta_n) \equiv (\tilde{\eta}_1 \tilde{\eta}_2 \cdots \tilde{\eta}_{2n}). \quad (3.112)$$

We write  $\tilde{\zeta}$  as the linear transformation of  $\tilde{\eta}$ :

$$\tilde{\zeta}_i = M_{ij} \tilde{\eta}_j, \quad (3.113)$$

where  $M$  is the transformation matrix. The only non-vanishing terms in (3.110) are those polynomial containing each  $\tilde{\zeta}_i$  as a factor, which we can write as  $p \prod_{i=1}^{2n} \tilde{\zeta}_i$ , where  $p$  is the interchanging factor. Now we write

$$\int d\zeta_1^* d\zeta_1 \cdots d\zeta_n^* d\zeta_n p \prod_{i=1}^{2n} \tilde{\zeta}_i = J \int d\eta_1^* d\eta_1 \cdots d\eta_n^* d\eta_n p \prod_{i=1}^{2n} \left( \sum_j M_{ij} \tilde{\eta}_j \right), \quad (3.114)$$

where  $J$  is left to be determined and the form of this  $J$  gives the rule of transformation. The left side of the above expression is just  $p(-1)^n$ , and the non-vanishing terms of the right side come

from the  $(2n)!$  distinct permutations  $P$  of the variables  $\{\tilde{\eta}_i\}$ . Thus we have

$$\begin{aligned}
p(-1)^n &= Jp \int d\eta_1^* d\eta_1 \cdots d\eta_n^* d\eta_n \prod_{i=1}^{2n} \left( \sum_j M_{ij} \tilde{\eta}_j \right) \\
&= Jp \int d\eta_1^* d\eta_1 \cdots d\eta_n^* d\eta_n \sum_P \prod_{i=1}^{2n} M_{iP_i} \tilde{\eta}_{P_i} \\
&= Jp \sum_P \prod_{i=1}^{2n} M_{iP_i} (-1)^P \int d\eta_1^* d\eta_1 \cdots d\eta_n^* d\eta_n (\tilde{\eta}_1 \tilde{\eta}_2 \cdots \tilde{\eta}_{2n}) \\
&= Jp \det M (-1)^n,
\end{aligned} \tag{3.115}$$

so that

$$J = (\det M)^{-1} = \left| \frac{\partial(\eta^*, \eta)}{\partial(\zeta^*, \zeta)} \right|. \tag{3.116}$$

Hence the transformation law for an integral under a change of variables is

$$\int d\zeta_1^* d\zeta_1 \cdots d\zeta_n^* d\zeta_n P(\zeta^*, \zeta) = \left| \frac{\partial(\eta^*, \eta)}{\partial(\zeta^*, \zeta)} \right| \int d\eta_1^* d\eta_1 \cdots d\eta_n^* d\eta_n P(\zeta^*(\eta^*, \eta), \zeta(\eta^*, \eta)). \tag{3.117}$$

It should be emphasized that the transformation law is given by the inverse of the Jacobian instead of the Jacobian for ordinary numbers.

Using this transformation law for a multidimensional integral over Grassmann variables, (3.109) can be proved by defining  $\rho_i = \eta_i - H_{ij}^{-1} \zeta_j$ ,  $\rho_i^* = \eta_i^* - H_{ij}^{-1*} \zeta_j^*$ , and diagonalizing  $H$  with an unitary transformation  $U$  with  $\xi_i = U_{ij}^{-1} \rho_j$  and  $\xi_i^* = U_{ij}^{-1*} \rho_j^*$ . Noticing that the Jacobian is unity, we have

$$\begin{aligned}
\int \left( \prod_{i=1}^n d\eta_i^* d\eta_i \right) e^{-\eta_i^* H_{ij} \eta_j + \zeta_i^* \eta_i + \eta_i^* \zeta_i} &= \int \left( \prod_{i=1}^n d\rho_i^* d\rho_i \right) e^{-\rho_i^* H_{ij} \rho_j + \zeta_i^* H_{ij}^{-1} \zeta_j} \\
&= \int \left( \prod_{i=1}^n d\xi_i^* d\xi_i \right) e^{-\sum_i h_i \xi_i^* \xi_i + \zeta_i^* H_{ij}^{-1} \zeta_j} \\
&= \left( \prod_{m=1}^n h_m \right) e^{\zeta_i^* H_{ij}^{-1} \zeta_j} \\
&= [\det H] e^{\zeta_i^* H_{ij}^{-1} \zeta_j},
\end{aligned} \tag{3.118}$$

here we have used the fact that a Gaussian integral for a single pair of conjugate Grassmann variables is just

$$\int d\xi^* d\xi e^{-\xi^* a \xi} = \int d\xi^* d\xi (1 - \xi^* a \xi) = a. \tag{3.119}$$

### 3.7 Coherent State Functional Integral Formalism

The partition function of a many body system is

$$Z = \text{Tr} e^{-\beta(\hat{H}-\mu\hat{N})}, \quad (3.120)$$

where  $\beta$  is the inverse of temperature,  $\hat{H}$  is the Hamiltonian,  $\mu$  is the chemical potential and  $\hat{N}$  is the particle number operator. According to (3.104), the partition function for fermions can be written as

$$Z = \int \left( \prod_{\alpha} d\xi_{\alpha}^* d\xi_{\alpha} \right) e^{-\sum_{\alpha} \xi_{\alpha}^* \xi_{\alpha}} \langle -\xi | e^{-\beta(\hat{H}-\mu\hat{N})} | \xi \rangle. \quad (3.121)$$

Now we split  $\beta$  into  $M$  slices that  $\beta = M\delta\tau$ , then the partition function becomes

$$Z = \int \left( \prod_{\alpha} d\xi_{\alpha}^* d\xi_{\alpha} \right) e^{-\sum_{\alpha} \xi_{\alpha}^* \xi_{\alpha}} \langle -\xi | \prod_{i=1}^M e^{-\delta\tau(\hat{H}-\mu\hat{N})} | \xi \rangle. \quad (3.122)$$

Inserting the identity (3.94) between every  $e^{-\delta\tau(\hat{H}-\mu\hat{N})}$  in the above expression gives

$$\begin{aligned} Z = & \int \left( \prod_{\alpha} d\xi_{\alpha}^* d\xi_{\alpha} \right) e^{-\sum_{\alpha} \xi_{\alpha}^* \xi_{\alpha}} \left( \prod_{i=1}^{M-1} \prod_{\alpha} d\xi_{i,\alpha}^* d\xi_{i,\alpha} \right) \left( \prod_{i=1}^{M-1} e^{-\sum_{\alpha} \xi_{i,\alpha}^* \xi_{i,\alpha}} \right) \\ & \times \langle -\xi | e^{-\delta\tau(\hat{H}-\mu\hat{N})} | \xi_{M-1} \rangle \langle \xi_{M-1} | \cdots | \xi_1 \rangle \langle \xi_1 | e^{-\delta\tau(\hat{H}-\mu\hat{N})} | \xi \rangle. \end{aligned} \quad (3.123)$$

and labeling  $-\xi$  as  $\xi_M$  we obtain

$$Z = \int \left( \prod_{i=1}^M \prod_{\alpha} d\xi_{i,\alpha}^* d\xi_{i,\alpha} \right) \left( \prod_{i=1}^M e^{-\sum_{\alpha} \xi_{i,\alpha}^* \xi_{i,\alpha}} \right) \left( \prod_{i=2}^M \langle \xi_i | e^{-\delta\tau(\hat{H}-\mu\hat{N})} | \xi_{i-1} \rangle \right) \langle \xi_1 | e^{-\delta\tau(\hat{H}-\mu\hat{N})} | -\xi_M \rangle. \quad (3.124)$$

In second quantization formalism, the Hamiltonian  $\hat{H}$  is a function of annihilation operators and creation operators  $\hat{H}(\hat{a}_{\alpha}^{\dagger}, \hat{a}_{\alpha})$ . Now for convenience, we require the Hamiltonian to be *normal ordered* that all creation operators are to the left of all annihilation operators in the product<sup>1</sup>. And the operator  $\hat{N}$  is just  $\sum_{\alpha} \hat{a}_{\alpha}^{\dagger} \hat{a}_{\alpha}$ . Now let  $M \rightarrow \infty$ , and correspondingly  $\delta\tau \rightarrow 0$ . Since the coherent states are eigenstates of annihilation operators, we can replace the operators by their eigenvalues

---

<sup>1</sup>If the Hamiltonian is not normal ordered, we should interchange the operators according to the commutation rule to make it be so.

when acting on coherent states, hence

$$\begin{aligned} \lim_{\tau \rightarrow 0} \langle \xi_i | e^{-\delta\tau(\hat{H}-\mu\hat{N})} | \xi_{i-1} \rangle &= \lim_{\tau \rightarrow 0} \langle \xi_i | 1 - \delta\tau[\hat{H}(\hat{a}_\alpha^\dagger, \hat{a}_\alpha) - \mu \sum_\alpha \hat{a}_\alpha^\dagger \hat{a}_\alpha] + O(\delta\tau^2) | \xi_{i-1} \rangle \\ &= \lim_{\tau \rightarrow 0} \langle \xi_i | e^{-\tau[H(\xi_{i,\alpha}^*, \xi_{i-1,\alpha}) - \mu \sum_\alpha \xi_{i,\alpha}^* \xi_{i-1,\alpha}]} | \xi_{i-1} \rangle + O(\delta\tau^2). \end{aligned} \quad (3.125)$$

Note that  $H(\xi_{i,\alpha}^*, \xi_{i-1,\alpha})$  is now not an operator but a function of Grassmann variables. With the above formula the equation (3.124) can be written as

$$\begin{aligned} Z &= \lim_{M \rightarrow \infty} \int \left( \prod_{i=1}^M \prod_\alpha d\xi_{i,\alpha}^* d\xi_{i,\alpha} \right) \left( \prod_{i=1}^M e^{-\sum_\alpha \xi_{i,\alpha}^* \xi_{i,\alpha}} \right) \\ &\quad \times \left( \prod_{i=2}^M \langle \xi_i | e^{-\delta\tau[H(\xi_{i,\alpha}^*, \xi_{i-1,\alpha}) - \mu \sum_\alpha \xi_{i,\alpha}^* \xi_{i-1,\alpha}]} | \xi_{i-1} \rangle \right) \langle \xi_1 | e^{-\delta\tau[H(\xi_{1,\alpha}^*, -\xi_{M,\alpha}) + \mu \sum_\alpha \xi_{1,\alpha}^* \xi_{M,\alpha}]} | -\xi_M \rangle, \end{aligned} \quad (3.126)$$

or, separating the exponential functions and the brackets,

$$\begin{aligned} Z &= \lim_{M \rightarrow \infty} \int \left( \prod_{i=1}^M \prod_\alpha d\xi_{i,\alpha}^* d\xi_{i,\alpha} \right) \left( \prod_{i=1}^M e^{-\sum_\alpha \xi_{i,\alpha}^* \xi_{i,\alpha}} \right) \left( \prod_{i=2}^M \langle \xi_i | \xi_{i-1} \rangle \right) \langle \xi_1 | -\xi_M \rangle \\ &\quad \times \left( \prod_{i=2}^M e^{-\delta\tau[H(\xi_{i,\alpha}^*, \xi_{i-1,\alpha}) - \mu \sum_\alpha \xi_{i,\alpha}^* \xi_{i-1,\alpha}]} \right) e^{-\delta\tau[H(\xi_{1,\alpha}^*, -\xi_{M,\alpha}) + \mu \sum_\alpha \xi_{1,\alpha}^* \xi_{M,\alpha}]}. \end{aligned} \quad (3.127)$$

Finally, collaborating with (3.93) we can write the partition function as

$$Z = \lim_{M \rightarrow \infty} \int \prod_{i=1}^M \prod_\alpha d\xi_{i,\alpha}^* d\xi_{i,\alpha} e^{-S(\xi^*, \xi)}, \quad (3.128)$$

where

$$\begin{aligned} S(\xi^*, \xi) &= \delta\tau \sum_{i=2} \left[ \sum_\alpha \xi_{i,\alpha}^* \left( \frac{\xi_{i,\alpha} - \xi_{i-1,\alpha}}{\delta\tau} - \mu \xi_{i-1,\alpha} \right) + H(\xi_{i,\alpha}^*, \xi_{i-1,\alpha}) \right] \\ &\quad + \delta\tau \left[ \sum_\alpha \xi_{1,\alpha}^* \left( \frac{\xi_{1,\alpha} + \xi_{M,\alpha}}{\delta\tau} + \mu \xi_{M,\alpha} \right) + H(\xi_{1,\alpha}^*, -\xi_{M,\alpha}) \right]. \end{aligned} \quad (3.129)$$

We may also write this expression for the partition symbolically as

$$Z = \int_{\xi_\alpha(\beta) = -\xi_\alpha(0)} D[\xi_\alpha^*(\tau) \xi_\alpha(\tau)] e^{-\int_0^\beta d\tau [\sum_\alpha \xi_\alpha^*(\tau) (\frac{\partial}{\partial \tau} - \mu) \xi_\alpha(\tau) + H(\xi_\alpha^*(\tau), \xi_\alpha(\tau))]}, \quad (3.130)$$

where the symbol  $\int D[\xi_\alpha^*(\tau) \xi_\alpha(\tau)]$  is understood as a functional integral over all possible tra-

jectories. Note that the Grassmann variables satisfy an anti-periodic boundary condition that  $\xi_\alpha(\beta) = -\xi_\alpha(0)$ . This is the *path integral* formalism for a Fermionic many body system.

### Partition Function for Non-Interacting Fermionic System

It is useful to give an example how to evaluate the path integral for Fermions. For convenience, we choose a non-interacting system with a diagonal Hamiltonian

$$\hat{H} = \sum_{\alpha} \varepsilon_{\alpha} \hat{a}_{\alpha}^{\dagger} \hat{a}_{\alpha} \quad (3.131)$$

as an example. Then the discrete expression for the partition function (3.128) may be written as

$$Z = \lim_{M \rightarrow \infty} \prod_{\alpha} \left[ \int \left( \prod_{i=1}^M d\xi_i^* d\xi_i \right) e^{-\sum_{ij} \xi_i^* S_{ij}^{(\alpha)} \xi_j} \right], \quad (3.132)$$

where the matrix  $S^{(\alpha)}$ , with the convention that time index  $\tau$  increases with increasing row and column index, is

$$S^{(\alpha)} = \begin{bmatrix} 1 & 0 & \cdots & 0 & a \\ -a & 1 & 0 & & 0 \\ 0 & -a & 1 & \ddots & \vdots \\ & 0 & -a & \ddots & 0 \\ \vdots & & 0 & \ddots & 1 & 0 \\ 0 & & & \cdots & -a & 1 \end{bmatrix}, \quad (3.133)$$

and

$$a = 1 - \delta\tau(\varepsilon_{\alpha} - \mu). \quad (3.134)$$

The expression for partition function (3.132) is a Gaussian integral over Grassmann variables, and collaborating with (3.109) yields

$$Z = \lim_{M \rightarrow \infty} \prod_{\alpha} \det S^{(\alpha)}. \quad (3.135)$$

The determinant of  $S^{(\alpha)}$  is

$$\begin{aligned}
\lim_{M \rightarrow \infty} \det S^{(\alpha)} &= \lim_{M \rightarrow \infty} [1 - (-1)^{M-1} (-a)^M] \\
&= \lim_{M \rightarrow \infty} \left[ 1 + \left( 1 - \frac{\beta(\varepsilon_\alpha - \mu)}{M} \right)^M \right] \\
&= 1 + e^{-\beta(\varepsilon_\alpha - \mu)},
\end{aligned} \tag{3.136}$$

and accordingly

$$Z = \prod_{\alpha} [1 + e^{-\beta(\varepsilon_\alpha - \mu)}]. \tag{3.137}$$

The Matsubara Green's function can be calculated in a similar manner. The Matsubara Green's function for a non-interacting Fermi system is defined as

$$G_{\alpha\gamma}(\tau_q, \tau_r) = -\frac{1}{Z} \text{Tr} \left[ e^{-\beta(\hat{H} - \mu \hat{N})} T_{\tau} \hat{a}_{\alpha}(\tau_q) \hat{a}_{\gamma}^{\dagger}(\tau_r) \right]. \tag{3.138}$$

Writing it in path integral form, then we have

$$\begin{aligned}
G_{\alpha\gamma}(\tau_q, \tau_r) &= -\frac{1}{Z} \lim_{M \rightarrow \infty} \prod_{\delta} \int \left( \prod_{i=1}^M d\xi_{i,\delta}^* d\xi_{i,\delta} \right) e^{-\sum_{i,j=1}^M \xi_{i,\delta}^* S_{ij}^{(\delta)} \xi_{i,\delta}} \xi_{q,\alpha} \xi_{r,\gamma}^* \\
&= -\delta_{\alpha\gamma} \frac{\int (\prod_i d\xi_i^* d\xi_i) e^{-\sum_{i,j=1}^M \xi_i^* S_{ij}^{(\alpha)} \xi_j}}{\int (\prod_i d\xi_i^* d\xi_i) e^{-\sum_{i,j=1}^M \xi_i^* S_{ij}^{(\alpha)} \xi_j}} \xi_q \xi_r^* \\
&= \delta_{\alpha\gamma} \frac{\partial^2}{\partial J_q^* \partial J_r} \frac{\int (\prod_i d\xi_i^* d\xi_i) e^{-\sum_{ij} \xi_i^* S_{ij}^{(\alpha)} \xi_j + \sum_i (J_i^* \xi_i + \xi_i^* J_i)}}{\int (\prod_i d\xi_i^* d\xi_i) e^{-\sum_{ij} \xi_i^* S_{ij}^{(\alpha)} \xi_j}} \Bigg|_{J=J^*=0} \\
&= \delta_{\alpha\gamma} \frac{\partial^2}{\partial J_q^* \partial J_r} e^{\sum_{ij} J_i^* S_{ij}^{(\alpha)-1} J_j} \Bigg|_{J=J^*=0} \\
&= -\delta_{\alpha\gamma} S^{(\alpha)-1}_{qr}.
\end{aligned} \tag{3.139}$$

The inverse matrix of  $S$  in (3.133), with  $a = 1 - \delta\tau(\varepsilon_\alpha - \mu)$ , is

$$S^{(\alpha)^{-1}} = \frac{1}{1+a^M} \begin{bmatrix} 1 & -a^{M-1} & -a^{M-2} & \dots & -a \\ a & 1 & -a^{M-1} & & -a^2 \\ a^2 & a & 1 & & \\ \vdots & a^2 & a & & \vdots \\ & & & a^2 & \\ a^{M-3} & & & & \\ a^{M-2} & a^{M-3} & & & -a^{M-1} \\ a^{M-1} & a^{M-2} & a^{M-3} & \dots & 1 \end{bmatrix}, \quad (3.140)$$

therefore for  $q \geq r$  we have

$$\begin{aligned} \lim_{M \rightarrow \infty} S^{(\alpha)^{-1}}_{qr} &= \lim_{M \rightarrow \infty} \frac{a^{q-r}}{1+a^M} \\ &= \lim_{M \rightarrow \infty} \left[ 1 - \frac{\beta}{M}(\varepsilon_\alpha - \mu) \right]^{q-r} \left[ 1 - \frac{1}{\left(1 - \frac{\beta}{M}(\varepsilon_\alpha - \mu)\right)^{-M} + 1} \right] \\ &= e^{-(\varepsilon_\alpha - \mu)(\tau_q - \tau_r)} \left[ 1 - \frac{1}{e^{\beta(\varepsilon_\alpha - \mu)} + 1} \right] \\ &= e^{-(\varepsilon_\alpha - \mu)(\tau_q - \tau_r)} (1 - n_\alpha), \end{aligned} \quad (3.141)$$

where  $n_\alpha$  is just the Fermi distribution

$$n_\alpha = \frac{1}{e^{\beta(\varepsilon_\alpha - \mu)} + 1}. \quad (3.142)$$

Similarly, if  $q \leq r$  we have

$$\begin{aligned} \lim_{M \rightarrow \infty} S^{(\alpha)^{-1}}_{qr} &= \lim_{M \rightarrow \infty} \frac{-a^{M+q-r}}{1+a^M} \\ &= \lim_{M \rightarrow \infty} \left[ 1 - \frac{\beta}{M}(\varepsilon_\alpha - \mu) \right]^{q-r} \frac{-1}{\left(1 - \frac{\beta}{M}(\varepsilon_\alpha - \mu)\right)^{-M} + 1} \\ &= -e^{-(\varepsilon_\alpha - \mu)(\tau_q - \tau_r)} n_\alpha. \end{aligned} \quad (3.143)$$

Hence the Matsubara Green's function is

$$G_{\alpha\gamma}(\tau_q, \tau_r) = \delta_{\alpha\gamma} \begin{cases} -e^{-(\varepsilon_\alpha - \mu)(\tau_q - \tau_r)}(1 - n_\alpha), & \tau_q \geq \tau_r; \\ e^{-(\varepsilon_\alpha - \mu)(\tau_q - \tau_r)}n_\alpha, & \tau_q < \tau_r. \end{cases} \quad (3.144)$$

Now let us return to the derivation of (3.36). The Hamiltonian of the impurity model is written as

$$\hat{H}_0 = \sum_{k\sigma} \varepsilon_k \hat{a}_{k\sigma}^\dagger \hat{a}_{k\sigma} - \mu \sum_{\sigma} \hat{c}_{\sigma}^\dagger \hat{c}_{\sigma} + \sum_{k\sigma} V_k (\hat{a}_{k\sigma}^\dagger \hat{c}_{\sigma} + \hat{c}_{\sigma}^\dagger \hat{a}_{k\sigma}), \quad (3.145)$$

and the corresponding partition function is

$$\begin{aligned} Z &= \text{Tr} e^{-\beta \hat{H}_0} \\ &= \int D[c_{\sigma}^*(\tau) c_{\sigma}(\tau)] \int D[a_{k\sigma}^*(\tau) a_{k\sigma}(\tau)] \\ &\quad e^{-\int_0^\beta d\tau [\sum_{k\sigma} a_{k\sigma}^*(\tau) \frac{\partial}{\partial \tau} a_{k\sigma}(\tau) + \sum_{\sigma} c_{\sigma}^*(\tau) (\frac{\partial}{\partial \tau} - \mu) c_{\sigma}(\tau) + \sum_{k\sigma} \varepsilon_k a_{k\sigma}^* a_{k\sigma} + \sum_k V_k (a_{k\sigma}^* c_{\sigma} + c_{\sigma}^* a_{k\sigma})]} \\ &= \int D[c_{\sigma}^*(\tau) c_{\sigma}(\tau)] e^{-\int_0^\beta d\tau \sum_{\sigma} c_{\sigma}^*(\tau) (\frac{\partial}{\partial \tau} - \mu) c_{\sigma}(\tau)} \\ &\quad \left[ \lim_{M \rightarrow \infty} \prod_{k\sigma} \int \left( \prod_{i=1}^M da_{k\sigma}^* da_{k\sigma} \right) e^{-\sum_{ij} a_i^* S_{ij}^{(k\sigma)} a_j - \sum_k (V_k a_{k\sigma}^* c_{\sigma} + c_{\sigma}^* a_{k\sigma})} \right], \end{aligned} \quad (3.146)$$

where the matrix  $S^{(k\sigma)}$  has the same form as (3.133) but with  $a = 1 - \delta\tau\varepsilon_{k\sigma}$ . Using the Grassmann Gaussian integral formula (3.109) the above formula becomes

$$Z = \int D[c_{\sigma}^*(\tau) c_{\sigma}(\tau)] e^{-\int_0^\beta d\tau \sum_{\sigma} c_{\sigma}^*(\tau) (\frac{\partial}{\partial \tau} - \mu) c_{\sigma}(\tau) + \int_0^\beta \int_0^\beta d\tau d\tau' \sum_{k\sigma} V_k^2 c_{\sigma}^*(\tau) S^{(k\sigma)-1} c_{\sigma}(\tau')}, \quad (3.147)$$

where the matrix  $S^{(k\sigma)-1}$  has the same form as (3.140) with  $a = 1 - \delta\tau\varepsilon_{k\sigma}$ . As the derivation of (3.139), the above form partition function can be written as a generating function for Green's functions as

$$Z = \int D[c_{\sigma}^*(\tau) c_{\sigma}(\tau)] e^{\int_0^\beta \int_0^\beta d\tau d\tau' \sum_{\sigma} c_{\sigma}^*(\tau) G_0^{-1}(\tau, \tau') c_{\sigma}(\tau')}. \quad (3.148)$$

Following the same procedures of deriving (3.141) and (3.143) we obtain that

$$G_0^{-1}(\tau, \tau') = \begin{cases} -\delta(\tau - \tau') (\frac{\partial}{\partial \tau} - \mu) + \sum_k V_k^2 \frac{e^{\varepsilon_k(\beta - \tau + \tau')}}{e^{\beta\varepsilon_k} + 1}, & \tau \geq \tau'; \\ -\delta(\tau - \tau') (\frac{\partial}{\partial \tau} - \mu) - \sum_k V_k^2 \frac{e^{-\varepsilon_k(\tau - \tau')}}{e^{\beta\varepsilon_k} + 1}, & \tau < \tau', \end{cases} \quad (3.149)$$



and applying a Fourier series on the range  $[0, \beta]$  we obtain

$$G_0^{-1}(i\omega_n) = i\omega_n + \mu - \sum_k \frac{V_k^2}{i\omega_n - \varepsilon_k}, \quad (3.150)$$

which coincides with (3.36).

### 3.8 Linked Cluster Theorem

In this section we shall briefly introduce the linked cluster theorem, which is needed when formally deriving dynamical mean-field theory. Let us consider a Hamiltonian consisting of a non-interacting term  $\hat{H}_0$  and a perturbation term  $\hat{V}$ :

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad (3.151)$$

where  $\hat{H}_0 = \sum_\alpha \varepsilon_\alpha \hat{a}_\alpha^\dagger \hat{a}_\alpha$  and  $\hat{V} = \hat{V}(\hat{a}^\dagger, \hat{a})$ . Then using path integral notation the partition function can be written as

$$\begin{aligned} Z &= \int_{\xi_\alpha(\beta) = -\xi_\alpha(0)} D[\xi_\alpha^*(\tau) \xi_\alpha(\tau)] e^{-\int_0^\beta d\tau [\sum_\alpha \xi_\alpha^*(\tau) (\frac{\partial}{\partial \tau} + \varepsilon_\alpha - \mu) \xi_\alpha(\tau) + V(\xi^*, \xi)]} \\ &= Z_0 \langle e^{-\int_0^\beta d\tau V(\xi^*, \xi)} \rangle_0, \end{aligned} \quad (3.152)$$

where the thermal average of a function  $F(\xi^*, \xi)$  is written

$$\langle F(\xi^*, \xi) \rangle_0 = \frac{1}{Z_0} \int_{\xi_\alpha(\beta) = -\xi_\alpha(0)} D[\xi_\alpha^*(\tau) \xi_\alpha(\tau)] e^{-\int_0^\beta d\tau \sum_\alpha \xi_\alpha^* (\frac{\partial}{\partial \tau} + \varepsilon_\alpha - \mu) \xi_\alpha} F(\xi^*, \xi). \quad (3.153)$$

Note that the time-ordering is implicit here since in path integral formalism the quantities are always time-ordered. And the partition function of the non-interacting Hamiltonian  $Z_0$ , when written in path integral form, is

$$Z_0 = \int_{\xi_\alpha(\beta) = -\xi_\alpha(0)} D[\xi_\alpha^*(\tau) \xi_\alpha(\tau)] e^{-\int_0^\beta d\tau \sum_\alpha \xi_\alpha^* (\frac{\partial}{\partial \tau} + \varepsilon_\alpha - \mu) \xi_\alpha}. \quad (3.154)$$

Accordingly the perturbation expansion can be obtained by expanding (3.152) in a power series

$$\frac{Z}{Z_0} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^\beta d\tau_1 \cdots d\tau_n \langle V(\xi^*(\tau_1), \xi(\tau_1)) \cdots V(\xi^*(\tau_n), \xi(\tau_n)) \rangle_0. \quad (3.155)$$

### Wick's Theorem

To evaluate the perturbation expansion, *Wick's theorem* [73] is used. In path integral form, the Wick's theorem corresponds to the following identity for integral of a product of Grassmann variables with a Gaussian:

$$\frac{\int D(\xi^* \xi) e^{-\sum_{ij} \xi_i^* M_{ij} \xi_j} \xi_{i_1} \xi_{i_2} \cdots \xi_{i_n} \xi_{j_1}^* \cdots \xi_{j_2}^* \xi_{j_1}^*}{\int D(\xi^* \xi) e^{-\sum_{ij} \xi_i^* M_{ij} \xi_j}} = \sum_P (-1)^P M_{i_{P_n}, j_n}^{-1} \cdots M_{i_{P_1}, j_1}^{-1}. \quad (3.156)$$

To prove this identity, we define a generating function

$$\begin{aligned} G(J^*, J) &= \frac{\int D(\xi^* \xi) e^{-\sum_{ij} \xi_i^* M_{ij} \xi_j + \sum_i (J_i^* \xi_i + \xi_i^* J_i)}}{\int D(\xi^* \xi) e^{-\sum_{ij} \xi_i^* M_{ij} \xi_j}} \\ &= e^{\sum_{ij} J_i^* M_{ij}^{-1} J_j}. \end{aligned} \quad (3.157)$$

Differentiation of this generating function with respect to the source  $J$  and  $J^*$  yields

$$\left. \frac{\delta^{2n} G}{\delta J_{i_1}^* \cdots \delta J_{i_n}^* \delta J_{j_n} \cdots \delta J_{j_1}} \right|_{J=J^*=0} = (-1)^n \frac{\int D(\xi^* \xi) e^{-\sum_{ij} \xi_i^* M_{ij} \xi_j} \xi_{i_1} \cdots \xi_{i_n} \xi_{j_n}^* \cdots \xi_{j_1}^*}{\int D(\xi^* \xi) e^{-\sum_{ij} \xi_i^* M_{ij} \xi_j}}, \quad (3.158)$$

note that here we have used the fact that all terms in the exponent are even in  $J$ 's and  $\xi$ 's and thus commute with  $\xi, \xi^*, J$  and  $J^*$ , and the factor  $(-1)^n$  comes from an odd number of interchanges for each differentiation with respect to  $J$ . However, differentiation of the generating function also yields

$$\begin{aligned} &\left. \frac{\delta^{2n}}{\delta J_{i_1}^* \cdots \delta J_{i_n}^* \delta J_{j_n} \cdots \delta J_{j_1}} (e^{\sum_{ij} J_i^* M_{ij}^{-1} J_j}) \right|_{J=J^*=0} \\ &= (-1)^n \frac{\delta^n}{\delta J_{i_1}^* \cdots \delta J_{i_n}^*} \left( \sum_{k_n} J_{k_n}^* M_{k_n j_n}^{-1} \right) \cdots \left( \sum_{k_1} J_{k_1}^* M_{k_1 j_1}^{-1} \right) e^{\sum_{ij} J_i^* M_{ij} J_j} \Bigg|_{J=J^*=0} \\ &= (-1)^n \sum_P (-1)^P M_{i_{P_n}, j_n}^{-1} \cdots M_{i_{P_1}, j_1}^{-1}. \end{aligned} \quad (3.159)$$

Equating (3.158) and (3.159) proves (3.156).

To apply Wick's theorem, first note that the Matsubara Green's function for a non-interacting system can be written as

$$\begin{aligned} G_{\alpha_1\alpha_2}^{(0)}(\tau_1, \tau_2) &= -\frac{\int D(\xi_i^* \xi) e^{-\int_0^\beta d\tau \sum_\alpha \xi_\alpha^* (\frac{\partial}{\partial \tau} + \varepsilon_\alpha - \mu) \xi_\alpha} \xi_{\alpha_1}(\tau_1) \xi_{\alpha_2}^*(\tau_2)}{\int D(\xi_i^* \xi) e^{-\int_0^\beta d\tau \sum_\alpha \xi_\alpha^* (\frac{\partial}{\partial \tau} + \varepsilon_\alpha - \mu) \xi_\alpha}} \\ &= -(\frac{\partial}{\partial \tau} + \varepsilon_\alpha - \mu)_{\alpha_1\tau_1; \alpha_2\tau_2}^{-1}, \end{aligned} \quad (3.160)$$

where  $(\frac{\partial}{\partial \tau} + \varepsilon_\alpha - \mu)$  is a symbol presenting the discrete matrix in the exponent and this matrix is used to replace  $M_{ij}$  in (3.156). Thus Wick's theorem shows that

$$\begin{aligned} &(-1)^n \langle \xi_{\alpha_1, i_1} \xi_{\alpha_2, i_2} \cdots \xi_{\alpha_n, i_n} \xi_{\gamma_n, j_n}^* \cdots \xi_{\gamma_2, j_2}^* \xi_{\gamma_1, j_1}^* \rangle_0 \\ &= \sum_P (-1)^P G_{\alpha_{P_n}, \gamma_{P_n}}^{(0)}(\tau_{i_{P_n}}, \tau_{j_{P_n}}) \cdots G_{\alpha_{P_1}, \gamma_{P_1}}^{(0)}(\tau_{i_{P_1}}, \tau_{j_{P_1}}) \\ &= \sum \text{all complete contractions.} \end{aligned} \quad (3.161)$$

For example,

$$\begin{aligned} &\langle \xi_{\alpha_1}(\tau_1) \xi_{\alpha_2}(\tau_2) \xi_{\alpha_3}^*(\tau_3) \xi_{\alpha_4}^*(\tau_4) \rangle_0 \\ &= \overbrace{\xi_{\alpha_1}(\tau_1) \xi_{\alpha_2}(\tau_2) \xi_{\alpha_3}^*(\tau_3) \xi_{\alpha_4}^*(\tau_4)} + \overbrace{\xi_{\alpha_1}(\tau_1) \xi_{\alpha_2}(\tau_2) \xi_{\alpha_3}^*(\tau_3) \xi_{\alpha_4}^*(\tau_4)} \\ &= G_{\alpha_1\alpha_4}^{(0)}(\tau_1, \tau_4) G_{\alpha_2\alpha_3}^{(0)}(\tau_2, \tau_3) - G_{\alpha_1\alpha_3}^{(0)}(\tau_1, \tau_3) G_{\alpha_2\alpha_4}^{(0)}(\tau_2, \tau_4). \end{aligned} \quad (3.162)$$

### Linked Cluster Theorem

With the Wick's theorem, the partition function  $Z$  can be expanded by Feynman diagrams as usual. In principle the expansion of  $Z$  contains both connected and disconnected diagrams. However, the linked cluster theorem states that  $\ln Z$  is given by the sum of all connected diagrams, and no disconnected diagram is involved.

We shall use the *replica technique* to derive this theorem. The basic idea of the replica method is to expand  $Z^n$  for integer  $n$  as

$$Z^n = e^{n \ln Z} = 1 + n \ln Z + \sum_{m=2}^{\infty} \frac{(n \ln Z)^m}{m!}. \quad (3.163)$$

And in the present case, we have

$$\lim_{n \rightarrow 0} \frac{d}{dn} Z^n = \lim_{n \rightarrow 0} \frac{d}{dn} (e^{n \ln Z}) = \ln Z. \quad (3.164)$$

We shall first evaluate  $Z^n$  by perturbation theory, and according to (3.163)  $\ln Z$  will be given by the coefficient of the diagrams proportional to  $n$ . Since the partition function  $Z$  can be written as

$$\frac{Z}{Z_0} = \frac{1}{Z_0} \int_{\xi_\alpha(\beta) = -\xi_\alpha(0)} D[\xi_\alpha^*(\tau) \xi_\alpha(\tau)] e^{-\int_0^\beta d\tau [\sum_\alpha \xi_\alpha^* (\frac{\partial}{\partial \tau} + \varepsilon_\alpha - \mu) \xi_\alpha(\tau) + V(\xi_\alpha^*(\tau), \xi_\alpha(\tau))]}, \quad (3.165)$$

we may write  $Z^n$  as a functional integral over  $n$  sets of  $\{\xi_\alpha^{\sigma*}(\tau), \xi_\alpha^\sigma(\tau)\}$  where the index  $\sigma$  runs from 1 to  $n$ :

$$\left(\frac{Z}{Z_0}\right)^n = \frac{1}{Z_0^n} \int_{\xi_\alpha^\sigma(\beta) = -\xi_\alpha^\sigma(0)} D[\xi_\alpha^{\sigma*}(\tau) \xi_\alpha^\sigma(\tau)] e^{-\int_0^\beta d\tau \sum_{\sigma=1}^n [\sum_\alpha \xi_\alpha^{\sigma*} (\frac{\partial}{\partial \tau} + \varepsilon_\alpha - \mu) \xi_\alpha^\sigma(\tau) + V(\xi_\alpha^{\sigma*}(\tau), \xi_\alpha^\sigma(\tau))]} \quad (3.166)$$

Now each propagator carries an index  $\sigma$ , all propagators entering or leaving a given vertex have the same index  $\sigma$ , and all  $\sigma$ 's are summed from 1 to  $n$ . It is clear that each connected part of a diagram must carry a single index  $\sigma$ , which when summed from 1 to  $n$ , gives a factor  $n$ . Thus a diagram with  $n_c$  connected parts has a factor proportional to  $n^{n_c}$  and the diagrams proportional to  $n$  are those with only one connected part, i.e. the connected diagrams.

In other words,  $\ln Z$  contains only the connected diagrams, this is the linked cluster theorem. It states that

$$\ln \frac{Z}{Z_0} = \sum (\text{all connected diagrams}). \quad (3.167)$$

Here we have only discussed the situation for the partition function, more details about linked cluster theorem can be found in Ref [72].

### 3.9 Derivation of the Dynamical Mean-Field Equations

In this section we shall use the Hubbard model as an example to derive the dynamical mean-field equations. The Hamiltonian of the Hubbard model can be written as

$$\hat{H} = \sum_{ij,\sigma} t_{ij} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} - \mu \hat{N}. \quad (3.168)$$

The dynamical mean-field theory becomes exact in the limit of infinity dimension. However, when dimension goes to infinite the kinetic energy of the Hubbard model becomes infinite accordingly, and the Coulomb interaction  $U$  can be then neglected. This would give a trivial result. In order to avoid this trivial result a scaled Hamiltonian is adopted, and such a scaled Hamiltonian is achieved by letting

$$t_{ij} = \frac{t}{\sqrt{2d}}, \quad (3.169)$$

where  $t$  is a constant for connected sites  $i, j$  and  $d$  is the dimension. It should be emphasized that this scaling is artificial. In a real situation we do not need to scale the Hamiltonian when applying dynamical mean-field theory. With this scaling the dynamical mean-field theory becomes exact at  $d \rightarrow \infty$  limit [74].

In this section we shall use the *cavity method*, which is borrowed from classical statistical mechanics, to derive the equations. Let us first demonstrate this on the *Ising model* [75]:

$$H = - \sum_{ij} J_{ij} S_i S_j - h \sum_i S_i. \quad (3.170)$$

The effective Hamiltonian  $H_{\text{eff}}$  for site  $o$  and is defined by the partial trace over all other spins:

$$\frac{1}{Z_{\text{eff}}} e^{-\beta \hat{H}_{\text{eff}}[S_o]} \equiv \frac{1}{Z} \sum_{S_i, i \neq o} e^{-\beta \hat{H}}. \quad (3.171)$$

The Hamiltonian  $H$  in (3.170) can be split into three terms as  $H = -h_o S_o - \sum_i J_{io} S_o S_i + H^{(o)}$ , where  $H^{(o)}$  is the Ising Hamiltonian in which the site  $o$  along with all bonds connecting site  $o$  are removed. Let  $\eta_i$  denote  $J_{io} S_o$ , which plays the role of a field acting on site  $i$ . Then the partition

function can be written as

$$\begin{aligned} Z &= \sum_{S_o} \exp(\beta h_o S_o) \sum_{S_i, i \neq o} \exp(-\beta \hat{H}^{(o)}) \exp\left(\beta \sum_i \eta_i S_i\right) \\ &= Z^{(o)} \sum_{S_o} \exp(\beta h_o S_o) \langle \exp\left(\beta \sum_i \eta_i S_i\right) \rangle^{(o)}, \end{aligned} \quad (3.172)$$

where  $\langle \dots \rangle^{(o)}$  means the average over  $H^{(o)}$ . The term  $\langle \exp(\beta \sum_i \eta_i S_i) \rangle^{(o)}$  can be expanded by products of  $S_i$ 's. Applying the linked cluster theorem and collecting only the connected terms we obtain an effective Hamiltonian which contains only connected diagrams:

$$H_{\text{eff}} = \text{const} + \sum_{n=1}^{\infty} \sum_{i_1 \dots i_n} \frac{1}{n!} \eta_{i_1} \dots \eta_{i_n} \langle S_{i_1} \dots S_{i_n} \rangle_c^{(o)}. \quad (3.173)$$

If the system is ferromagnetic, i.e.  $J_{ij} > 0$ , then to apply the Weiss mean-field theory in infinite dimension we need to scale  $J_{ij}$  as  $1/d^{|i-j|}$ . This scaling, of course, is also artificial in order to avoid trivial solution. And  $|i-j|$  is the Manhattan distance<sup>2</sup> between  $i$  and  $j$ . With such a scaling, only the first term ( $n=1$ ) survives in the expression in the  $d \rightarrow \infty$  limit, hence we have

$$H_{\text{eff}} = -h_{\text{eff}} S_o, \quad (3.174)$$

where

$$h_{\text{eff}} = h + \sum_i J_{oi} \langle S_i \rangle^{(o)}. \quad (3.175)$$

$\langle S_i \rangle^{(o)}$  is the magnetization at site  $i$  with site  $o$  removed. Since each site has infinite neighbors when  $d \rightarrow \infty$ , removing one of them does not affect at all. This, together with the transitional invariance, implies that  $\langle S_i \rangle = \langle S_o \rangle \equiv m$ , so  $h_{\text{eff}} = h + zJm$  with  $z$  to be the number of neighbors. Thus we obtain the Weiss mean-field equations for the Ising model.

This derivation can be extended in a straightforward manner to the Hubbard model. The partition function can be written in a functional integral form as

$$Z = \int D[c_{i\sigma}^*(\tau) c_{i\sigma}(\tau)] e^{-S}, \quad (3.176)$$

---

<sup>2</sup>Manhattan distance is also called taxicab metric, which is defined as the number of bonds of the shortest path connecting  $i$  and  $j$ .

where

$$S = \int_0^\beta d\tau \left( \sum_{i\sigma} c_{i\sigma}^* \partial_\tau c_{i\sigma} + \sum_{ij,\sigma} t_{ij} c_{i\sigma}^* c_{i\sigma} - \mu \sum_{i\sigma} n_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \right) \quad (3.177)$$

Here for convenience the Grassmann variables are denoted by  $c^*$  and  $c$ . We follow the Ising analogy: the sites are traced out except site  $o$  in order to obtain the effective action:

$$\frac{1}{Z_{\text{eff}}} e^{-S_{\text{eff}}[c_{o\sigma}^*, c_{o\sigma}]} = \frac{1}{Z} \int \prod_{i \neq o, \sigma} D[c_{i\sigma}^* c_{i\sigma}] e^{-S}. \quad (3.178)$$

In order to obtain this effective action  $S_{\text{eff}}$ , we split the original action  $S$  into three parts as  $S = S^{(o)} + S_o + \Delta S$ , where  $S^{(o)}$  is the lattice action without site  $o$  and

$$S_o = \int_0^\beta d\tau \left[ \sum_\sigma c_{o\sigma}^* (\partial_\tau - \mu) c_{o\sigma} + U n_{o\uparrow} n_{o\downarrow} \right], \quad \Delta S = \int_0^\beta d\tau \sum_{i\sigma} t_{io} (c_{i\sigma}^* c_{o\sigma} + c_{o\sigma}^* c_{i\sigma}). \quad (3.179)$$

Now denote  $t_{io} c_{o\sigma}$  by  $\eta_i$ , then the partition function can be written as

$$\begin{aligned} Z &= \int D[c_{o\sigma}^* c_{o\sigma}] e^{-S_o} \int \prod_{i \neq o} D[c_{i\sigma}^* c_{i\sigma}] e^{-S^{(o)}} e^{-\Delta S} \\ &= Z^{(o)} \int D[c_{o\sigma}^* c_{o\sigma}] e^{-S_o} \langle e^{-\Delta S} \rangle^{(o)}. \end{aligned} \quad (3.180)$$

According to the linked cluster theorem, the above expression gives the generating functional of the connected Green's function  $G^{(o)}$  of the cavity Hamiltonian  $\hat{H}^{(o)}$ :

$$\begin{aligned} S_{\text{eff}} &= \sum_{n=1}^{\infty} \sum_{i_1 \dots i_n} \sum_{j_1 \dots j_n} \int d\tau_{i_1} \dots d\tau_{j_n} \eta_{i_1}^*(\tau_{i_1}) \dots \eta_{i_n}^*(\tau_{i_n}) \eta_{j_1}(\tau_{j_1}) \dots \eta_{j_n}(\tau_{j_n}) \\ &\quad \times G_{i_1 \dots j_n}^{(o)}(\tau_{i_1} \dots \tau_{i_n}, \tau_{j_1} \dots \tau_{j_n}) + S_o + \text{const}. \end{aligned} \quad (3.181)$$

The scaling of the hopping  $t_{ij}$  is  $1/\sqrt{d}^{|i-j|}$ , and this scaling brings a crucial simplification. The  $n$ th order term is of order  $(1/d)^{n-1}$  so that only the  $n = 1$  term survives in the  $d \rightarrow \infty$  limit. This can be seen from the first few terms. The scaling of  $t_{ij}$  ensures that  $G_{ij}^{(o)} \sim (1/\sqrt{d})^{|i-j|}$  so the first term is of order 1. The second-order term contains a connected four-point Green's function  $G_{ijkl}^{(o)}$  which gives  $(1/\sqrt{d})^{|i-k|} (1/\sqrt{d})^{|i-l|} (1/\sqrt{d})^{|j-k|} (1/\sqrt{d})^{|j-l|}$ . When  $i, j, k, l$  are all different, there are four sums which give a  $d^4$  factor and four  $t$  give  $1/d^2$ . And since the sum of  $|i-k|$ ,  $|i-j|$ ,  $|j-k|$  and  $|j-l|$  are at least 6, the net result is of order  $1/d$ , which vanishes in the  $d \rightarrow \infty$  limit. Thus

we have

$$S_{\text{eff}} = \text{const} + S_o + \sum_{ij} \int \eta_i^*(\tau_i) \eta_j(\tau_j) G_{ij}^{(o)}(\tau_i, \tau_j). \quad (3.182)$$

The constant in  $S_{\text{eff}}$  cancels with  $1/Z_{\text{eff}}$ , thus explicitly we have

$$S_{\text{eff}} = \int_0^\beta d\tau \left[ \sum_\sigma c_{o\sigma}^* (\partial_\tau - \mu) c_{o\sigma} + U n_{o\uparrow} n_{o\downarrow} \right] + \sum_{ij} \int_0^\beta t_{io} t_{oj} c_{io}^*(\tau_i) G_{ij}^{(o)}(\tau_i, \tau_j) c_{oj}(\tau_j) d\tau_i d\tau_j. \quad (3.183)$$

Now we can write  $S_{\text{eff}}$  in the form

$$S_{\text{eff}} = - \int_0^\beta d\tau d\tau' \sum_\sigma c_{o\sigma}^*(\tau) G_0^{-1}(\tau - \tau') c_{o\sigma}(\tau') + U \int_0^\beta d\tau n_{o\uparrow}(\tau) n_{o\downarrow}(\tau), \quad (3.184)$$

with

$$G_0^{-1}(i\omega_n) = i\omega_n + \mu - \sum_{ij} t_{io} t_{jo} G_{ij}^{(o)}(i\omega_n). \quad (3.185)$$

This  $G_0$  acts as the mean-field function and contains the information of environment. The expression (3.185) relates the mean-field function  $G_0$  and the cavity Green's function  $G^{(o)}$ . In order to obtain a close set of equations, we still need to relate  $G^{(o)}$  to the original Green's function. For a general lattice, the relation between the cavity and full Green's function is [55, 76]

$$G_{ij}^{(o)} = G_{ij} - \frac{G_{io} G_{oj}}{G_{oo}}. \quad (3.186)$$

Substituting (3.186) into (3.185) we obtain

$$G_0^{-1}(i\omega_n) = i\omega_n + \mu + \sum_{ij} t_{io} t_{oj} G_{ij} - \left( \sum_i t_{io} G_{io} \right)^2 / G_{oo}. \quad (3.187)$$

The hopping term  $t_{io}$  and the Green's function  $G_{ij}$  can be Fourier transformed into  $\mathbf{k}$  space, and thus the above expression can be written as

$$G_0^{-1}(i\omega_n) = i\omega_n + \mu - \int d\varepsilon \frac{\rho(\varepsilon) \varepsilon^2}{\zeta - \varepsilon} + \left[ \int d\varepsilon \frac{\rho(\varepsilon) \varepsilon}{\zeta - \varepsilon} \right]^2 / \int d\varepsilon \frac{\rho(\varepsilon)}{\zeta - \varepsilon} \quad (3.188)$$

with  $\zeta = i\omega_n + \mu - \Sigma(i\omega_n)$  and  $\rho$  the density of states. This expression can be simplified further



using the following relations:

$$\int d\varepsilon \frac{\rho(\varepsilon)\varepsilon^2}{\zeta - \varepsilon} = \zeta \int d\varepsilon \frac{\rho(\varepsilon)\varepsilon}{\zeta - \varepsilon}, \quad \int d\varepsilon \frac{\rho(\varepsilon)\varepsilon}{\zeta - \varepsilon} = -1 + \zeta \int d\varepsilon \frac{\rho(\varepsilon)}{\zeta - \varepsilon}. \quad (3.189)$$

Recalling that  $G(i\omega_n) = \int \rho(\varepsilon)/(\zeta - \varepsilon)$  finally we obtain that

$$\Sigma(i\omega_n) = G_0^{-1}(i\omega_n) - G^{-1}(i\omega_n). \quad (3.190)$$



## Chapter 4

# Dynamical Mean-Field Theory for Small Polaron

Conduction electrons interact with the vibrating atoms in the lattice. If this interaction is strong enough, the electron can cause a local deformation of the lattice, and this deformation would create a potential well which, in turn, binds the electron. This phenomenon is called *self-trapping* and was first introduced by Lev Landau in 1933 [90]. Later, Solomon Pekar [91] proposed another physical picture: the electron and the deformation (phonon cloud) created by it together form a new quasi-particle which is called *polaron*.

Polarons are important to understand a wide variety of materials in experiments. The electron mobility can be greatly decreased by the formation of polarons. Polaronic interaction is also important in magnetoresistance effects of various materials [3–11].

Until now, the polaron problem is an old but not fully solved problem. It is still an active field of research to find good numerical solutions. In this chapter we shall focus on the *small polaron* problem and introduce the corresponding dynamical mean-field theory [92, 93].

### 4.1 Impurity Model at Zero Temperature

As in the dynamical mean-field theory for the Hubbard model discussed in the last chapter, the essential part is the impurity model. In this section we shall discuss a simple impurity model for electrons at zero temperature, which is needed when we deal with the dynamical mean-field theory

for small polaron.

The Hamiltonian of this simple impurity model is defined as

$$\hat{H} = \sum_k \varepsilon_k \hat{c}_k^\dagger \hat{c}_k + \sum_k V_k (\hat{c}_k^\dagger \hat{d} + \hat{d}^\dagger \hat{c}_k) + \varepsilon_0 \hat{d}^\dagger \hat{d}, \quad (4.1)$$

where  $\hat{c}_k^\dagger$  ( $\hat{c}_k$ ) represents a creation (annihilation) operator in the electron bath and  $\hat{d}^\dagger$  ( $\hat{d}$ ) is the creation (annihilation) operator in the impurity. Now write the Hamiltonian in two parts as

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad (4.2)$$

where

$$\hat{H}_0 = \sum_k \varepsilon_k \hat{c}_k^\dagger \hat{c}_k + \varepsilon_0 \hat{d}^\dagger \hat{d}, \quad \hat{V} = \sum_k V_k (\hat{c}_k^\dagger \hat{d} + \hat{d}^\dagger \hat{c}_k). \quad (4.3)$$

Now we define a retarded Green's function for the impurity as

$$\begin{aligned} G(t) &= -i\theta(t) \langle 0 | \hat{d}(t) \hat{d}^\dagger + \hat{d}^\dagger \hat{d}(t) | 0 \rangle \\ &= -i \langle 0 | \hat{d}(t) \hat{d}^\dagger | 0 \rangle, \quad t \geq 0. \end{aligned} \quad (4.4)$$

Applying a Fourier transform to the Green's function then

$$G(\omega) = \langle 0 | \hat{d} \frac{1}{\omega + i0 - \hat{H}} \hat{d}^\dagger | 0 \rangle. \quad (4.5)$$

Note that  $1/(\omega - \hat{H})$  can be written as

$$\begin{aligned} \frac{1}{\omega - \hat{H}} &= \frac{1}{\omega - \hat{H}_0} + \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}} \\ &= \frac{1}{\omega - \hat{H}_0} + \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}_0} + \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}}, \end{aligned} \quad (4.6)$$

thus we have

$$G(\omega) = \langle 0 | \frac{1}{\omega - \hat{H}_0} | 0 \rangle + \langle 0 | \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}} | 0 \rangle + \langle 0 | \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}} | 0 \rangle. \quad (4.7)$$

It is easy to see that the second term in the above expression is just zero, then we have

$$\begin{aligned}
 G(\omega) &= \langle 0 | \frac{1}{\omega - \hat{H}_0} | 0 \rangle + \langle 0 | \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}} | 0 \rangle \\
 &= \frac{1}{\omega - \varepsilon_0} + \frac{1}{\omega - \varepsilon_0} \langle 0 | \hat{d} \hat{V} \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}} \hat{d}^\dagger | 0 \rangle \\
 &= \frac{1}{\omega - \varepsilon_0} + \frac{1}{\omega - \varepsilon_0} \langle 0 | \hat{d} \sum_k \hat{d}^\dagger \hat{c}_k \frac{V_k^2}{\omega - \hat{H}_0} \hat{c}_k^\dagger \hat{d} \frac{1}{\omega - \hat{H}} \hat{d}^\dagger | 0 \rangle \\
 &= \frac{1}{\omega - \varepsilon_0} + \frac{1}{\omega - \varepsilon_0} \sum_k \frac{V_k^2}{\omega - \varepsilon_k} G(\omega).
 \end{aligned} \tag{4.8}$$

Therefore the inverse of the Green's function is

$$G^{-1}(\omega) = \omega - \varepsilon_0 - \sum_k \frac{V_k^2}{\omega - \varepsilon_k}, \tag{4.9}$$

which can be written as

$$G^{-1}(\omega) = \omega - \varepsilon_0 - \int_{-\infty}^{\infty} d\varepsilon \frac{\Delta(\varepsilon)}{\omega - \varepsilon} \tag{4.10}$$

with

$$\Delta(\varepsilon) = \sum_k V_k^2 \delta(\varepsilon - \varepsilon_k). \tag{4.11}$$

This expression is similar to the formal expression (3.36) of the unperturbed Matsubara Green's function for an impurity model.

## 4.2 The Impurity Solver for the Holstein Model: Zero Temperature Formalism

The *Holstein model* [94, 95] was introduced in the 1950s to study the small polaron problem. In this model, tight-binding electrons interact with local dispersionless optical phonon. Although this is a rather crude idealization of real materials, the Holstein model captures the essential physical mechanism of small polaron.

The Hamiltonian of the Holstein model is

$$\hat{H} = \sum_{ij} t_{ij} \hat{c}_i^\dagger \hat{c}_j + g \sum_i \hat{c}_i^\dagger \hat{c}_i (\hat{a}_i + \hat{a}_i^\dagger) + \omega_0 \sum_i \hat{a}_i^\dagger \hat{a}_i, \tag{4.12}$$

where  $\hat{c}_i^\dagger$  ( $\hat{c}_i$ ) creates (destroys) an electron at site  $i$ , and  $\hat{a}_i^\dagger$  ( $\hat{a}_i$ ) creates (destroys) a phonon at site  $i$ . The frequency of the dispersionless optical phonon is denoted by  $\omega_0$  and the electron-phonon interaction strength is denoted by  $g$ . Similarly to what we have done for the Hubbard model, the Hamiltonian of Holstein model can also be split into three parts: bath, impurity and hybridization term, and formally be rewritten as

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad (4.13)$$

where

$$\hat{H}_0 = \sum_k \varepsilon_k \hat{c}_k^\dagger \hat{c}_k + \sum_k V_k (\hat{c}_k^\dagger \hat{d} + \hat{d}^\dagger \hat{c}_k) + \omega_0 \hat{a}^\dagger \hat{a} \quad (4.14)$$

with  $\hat{c}_k^\dagger, \hat{c}_k$  the electron operators in the bath,  $\hat{d}^\dagger, \hat{d}$  the electron operator in the impurity and  $\hat{a}^\dagger, \hat{a}$  the phonon operator in the impurity. And

$$\hat{V} = g \hat{d}^\dagger \hat{d} (\hat{a} + \hat{a}^\dagger) \quad (4.15)$$

represents the electron-phonon interaction at the impurity. Then, formally solving  $\hat{H}_0$  yields an unperturbed Green's function

$$G^{(0)}(\omega) = \langle 0 | \hat{d} \frac{1}{\omega + i0 - \hat{H}_0} \hat{d}^\dagger | 0 \rangle. \quad (4.16)$$

In this section we consider the zero temperature formalism, therefore the Green's function and its Fourier transform are defined as

$$G(t) = -i\theta(t) \langle 0 | \hat{d}(t) \hat{d}^\dagger | 0 \rangle, \quad G(\omega) = \langle 0 | \hat{d} \frac{1}{\omega + i0 - \hat{H}} \hat{d}^\dagger | 0 \rangle. \quad (4.17)$$

To proceed further, we need to introduce generalized matrix elements for the Green's function as

$$G_{nm}(\omega) = \langle 0 | \frac{\hat{a}}{\sqrt{n!}} \hat{d} \frac{1}{\omega - \hat{H}} \hat{d}^\dagger \frac{(\hat{a}^\dagger)^m}{\sqrt{m!}} | 0 \rangle. \quad (4.18)$$

Now introduce a set of zero electron  $p$ -phonon states and a set of one electron  $p$ -phonon states

$$|0, p\rangle = \frac{(\hat{a}^\dagger)^p}{\sqrt{p!}} |0\rangle, \quad |1, p\rangle = \frac{(\hat{a}^\dagger)^p}{\sqrt{p!}} \hat{d}^\dagger |0\rangle, \quad (4.19)$$

and then we can write

$$G_{nm}(\omega) = \langle 0, n | \hat{d} \frac{1}{\omega - \hat{H}} \hat{d}^\dagger | 0, m \rangle. \quad (4.20)$$

Recalling that

$$\frac{1}{\omega - \hat{H}} = \frac{1}{\omega - \hat{H}_0} + \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}} \quad (4.21)$$

we can write

$$\begin{aligned} G_{nm}(\omega) &= \langle 0, n | \hat{d} \frac{1}{\omega - \hat{H}_0} \hat{d}^\dagger | 0, m \rangle + \langle 0, n | \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}} | 0, m \rangle \\ &= G_{nm}^{(0)} + g \sum_{p_1, p_2} \langle 0, n | \hat{d} \frac{1}{\omega - \hat{H}_0} \hat{d}^\dagger | 0, p_1 \rangle \langle 0, p_1 | \hat{d}(\hat{a} + \hat{a}^\dagger) \hat{d}^\dagger | 0, p_2 \rangle \langle 0, p_2 | \hat{d} \frac{1}{\omega - \hat{H}} \hat{d}^\dagger | 0, m \rangle \\ &= G_{nm}^{(0)} + g \sum_{p_1, p_2} G_{n, p_1}^{(0)} X_{p_1, p_2} G_{p_2, m}. \end{aligned} \quad (4.22)$$

This is just the Dyson equation and it can be written in matrix form as

$$G = G^{(0)} + gG^{(0)}XG \quad \text{or} \quad G^{-1} = [G^{(0)}]^{-1} - gX, \quad (4.23)$$

where  $X$  is the phonon displacement matrix with the elements

$$X_{np} = \sqrt{p+1} \delta_{n, p+1} + \sqrt{p} \delta_{n, p-1}. \quad (4.24)$$

According to the discussion in the previous section, the generalized unperturbed Green's function matrix elements are

$$\begin{aligned} G_{nm}^{(0)}(\omega) &= \langle 0, n | \hat{d} \frac{1}{\omega + i0 - \hat{H}_0} \hat{d}^\dagger | 0, m \rangle \\ &= \left[ \omega - n\omega_0 - \sum_k \frac{V_k^2}{\omega - \varepsilon_k} \right]^{-1} \delta_{nm} \\ &= \delta_{nm} G_{00}^{(0)}(\omega - n\omega_0). \end{aligned} \quad (4.25)$$

It is easy to see that  $G^{(0)}$  and  $[G^{(0)}]^{-1}$  are diagonal matrices and  $X$  is a tridiagonal matrix, and

$G^{-1}$  is also a tridiagonal matrix:

$$G^{-1} = \begin{pmatrix} [G_{00}^{(0)}]^{-1} & -g & 0 & \cdots & \cdots \\ -g & [G_{11}^{(0)}]^{-1} & -\sqrt{2}g & \cdots & \cdots \\ 0 & -\sqrt{2}g & [G_{22}^{(0)}]^{-1} & -\sqrt{3}g & \cdots \\ 0 & 0 & -\sqrt{3}g & [G_{33}^{(0)}]^{-1} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \quad (4.26)$$

In principle, the Green's function matrix  $G$  can be obtained by solving an algebra equation  $G^{-1}G = I$  and the first element in the matrix  $G_{00}$  is what we want. Now define a quantity  $T_k$  as the determinant of  $G^{-1}$  with first  $k$  rows and columns removed, then according to Cramer's rule we have

$$G_{00} = \frac{T_1}{T_0}. \quad (4.27)$$

From the explicit matrix form (4.26) we can find a recursive relation of  $T_k$  that

$$T_k = [G^{(0)}]_{kk}^{-1} T_{k+1} - (k+1) T_{k+2}, \quad (4.28)$$

or

$$\frac{T_k}{T_{k+1}} = [G_{kk}^{(0)}]^{-1} - (k+1)g^2 \frac{T_{k+2}}{T_{k+1}}, \quad (4.29)$$

thus we have

$$\frac{T_1}{T_0} = \frac{1}{[G_{00}^{(0)}]^{-1} - g^2 \frac{T_2}{T_1}}. \quad (4.30)$$

Expanding the above expression recursively we shall obtain a *continued-fraction expansion* for the Green's function  $G(\omega)$ :

$$G(\omega) = G_{00}(\omega) = \frac{1}{[G^{(0)}(\omega)]^{-1} - \frac{g^2}{[G^{(0)}(\omega - \omega_0)]^{-1} - \frac{2g^2}{[G^{(0)}(\omega - 2\omega_0)]^{-1} - \frac{3g^2}{[G^{(0)}(\omega - 3\omega_0)]^{-1} - \cdots}}}} \quad (4.31)$$



and the expression for the self-energy  $\Sigma = [G^{(0)}]^{-1} - G^{-1}$ :

$$\Sigma(\omega) = \frac{g^2}{[G^{(0)}(\omega - \omega_0)]^{-1} - \frac{2g^2}{[G^{(0)}(\omega - 2\omega_0)]^{-1} - \frac{3g^2}{[G^{(0)}(\omega - 3\omega_0)]^{-1} - \dots}} \quad (4.32)$$

This form of self-energy can be defined recursively as

$$\Sigma^{(p)}(\omega) = \frac{pg^2}{[G^{(0)}(\omega - p\omega_0)]^{-1} - \Sigma^{(p+1)}}. \quad (4.33)$$

Finally we obtain an analytic continued-fraction expansion formula for impurity solver. Such an impurity solver allows us to use retarded Green's function, rather than Matsubara Green's function, to do the dynamical mean-field theory calculation. This is a crucial advantage of such an impurity solver. More details about the recursion technique used here can be found in Ref [96].

### 4.3 The Impurity Solver for Holstein Model: Finite Temperature Formalism

The zero temperature formalism of the impurity solver for the Holstein model can be easily generalized to finite temperature. Here, a fundamental assumption has to be made: since only one electron is considered, the temperature would not affect the electron. In other words, when dealing with electron the temperature still remains zero, and the effect of temperature enters only in the phonons. Thus the trace over the canonical distribution of phonon states gives the expression for the Green's function at finite temperature as

$$G(\omega) = (1 - e^{\beta\omega_0}) \sum_n e^{-\beta n\omega_0} G_{nn}(\omega), \quad (4.34)$$

where  $\beta = 1/T$ .

It is clear that in order to obtain  $G(\omega)$  we need to calculate  $G_{nn}(\omega)$ . Since  $G^{-1}$  is a tridiagonal matrix, according to the equation  $G^{-1}G = I$  we have a recursive relation that

$$G_{nn} = G_{nn}^{(0)} + gG_{nn}^{(0)}(\sqrt{n}G_{n-1,n} + \sqrt{n+1}G_{n+1,n}), \quad (4.35)$$

where  $G_{-1,0}$  and  $G_{0,-1}$  are defined to be zero. Now we seek to write this expression in a form as

$$G_{nn} = G^{(0)} + G^{(0)}(AG_{nn} + BG_{nn}). \quad (4.36)$$

Define a quantity  $D_k$  as the determinant comprising the first  $k + 1$  rows and columns of  $G^{-1}$  and  $D_{-1} = 1, D_{-2} = 0$ , then it is easy to find that

$$\begin{aligned} D_0 &= [G_{00}^{(0)}]^{-1}, \\ D_1 &= [G_{11}^{(0)}]^{-1}[G_{11}^{(0)}]^{-1} - g^2 = [G_{11}^{(0)}]^{-1}D_0 - g^2, \\ D_2 &= \dots = [G_{22}^{(0)}]^{-1}D_1 - 2g^2D_0, \end{aligned} \quad (4.37)$$

and so on. In general, a recursive relation is obtained that

$$D_k = [G_{kk}^{(0)}]^{-1}D_{k-1} - kg^2D_{k-2}. \quad (4.38)$$

Using Cramer's rule again we obtain the expressions

$$G_{n-1,n} = \sqrt{n}g \frac{D_{n-2}T_{n+1}}{T_0}, \quad G_{nn} \frac{D_{n-1}T_{n+1}}{T_0}, \quad G_{n+1,n} = \sqrt{n+1}g \frac{D_{n-1}T_{n+2}}{T_0}. \quad (4.39)$$

The recursive relation (4.38) can be written as

$$\frac{D_{k-1}}{D_k} = \frac{1}{[G_{kk}^{(0)}]^{-1} - kg^2 \frac{D_{k-2}}{D_{k-1}}}, \quad (4.40)$$

and substituting this expression into (4.39) yields

$$G_{n-1,n} = \sqrt{n}g \frac{D_{n-2}}{D_{n-1}} \frac{D_{n-1}T_{n+1}}{T_0} = \sqrt{n}g \frac{D_{n-2}}{D_{n-1}} G_{nn}, \quad (4.41)$$

i.e.,

$$A = ng^2 \frac{D_{n-2}}{D_{n-1}} = \frac{ng^2}{[G_{nn}^{(0)}(\omega + \omega_0)]^{-1} - \frac{(n-1)g^2}{[G_{nn}^{(0)}(\omega + 2\omega_0)]^{-1} - \frac{(n-2)g^2}{g^2} \dots - [G_{nn}^{(0)}(\omega + n\omega_0)]^{-1}}}. \quad (4.42)$$

Note that this expression for  $A$  is a finite continued-fraction expansion. Following a similar approach, we have

$$G_{n+1,n} = \sqrt{n+1}g \frac{D_{n-1}T_{n+2}}{T_0} = \sqrt{n+1}g \frac{T_{n+2}}{T_{n+1}} G_{nn}. \quad (4.43)$$

The recursive relation (4.28) of  $T_k$  can be written as

$$\frac{T_{k+1}}{T_k} = \frac{1}{[G_{kk}^{(0)}]^{-1} - (k+1)g^2 \frac{T_{k+2}}{T_{k+1}}}, \quad (4.44)$$

therefore we have

$$B = (n+1)g^2 \frac{T_{n+2}}{T_{n+1}} = \frac{(n+1)g^2}{[G_{nn}^{(0)}(\omega - \omega_0)]^{-1} - \frac{(n+2)g^2}{[G_{nn}^{(0)}(\omega - 2\omega_0)]^{-1} - \frac{(n+3)g^2}{[G_{nn}^{(0)}(\omega - 3\omega_0)]^{-1} - \dots}}. \quad (4.45)$$

This expression is an infinite continued-fraction expansion. Finally we obtain the expression for  $G_{nn}$ :

$$G_{nn} = \frac{1}{[G_{nn}^{(0)}]^{-1} - A - B}. \quad (4.46)$$

## 4.4 Dynamical Mean-Field Equations

Following the same procedure of deriving dynamical mean-field equations for the Hubbard model, we can derive the corresponding equations for the small polaron. We use the cavity method again. Now choose a site  $o$  as the impurity and consider  $\hat{V}$  in real space representation as

$$\hat{V} = \sum_i (t_{io} \hat{c}_i^\dagger \hat{d} + t_{oi} \hat{d}^\dagger \hat{c}_i). \quad (4.47)$$

In this representation, the Green's function  $G(\omega)$  becomes

$$\begin{aligned} G(\omega) &= \langle 0 | \hat{d} \frac{1}{\omega - \hat{H}_0} \hat{d}^\dagger | 0 \rangle + \langle 0 | \hat{d} \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}_0} \hat{V} \frac{1}{\omega - \hat{H}} \hat{d}^\dagger | 0 \rangle \\ &= \langle 0 | \hat{d} \frac{1}{\omega - \hat{H}_0} \hat{d}^\dagger | 0 \rangle + \sum_{ij} t_{io} t_{oj} \langle 0 | \hat{d} \frac{1}{\omega - \hat{H}_0} \hat{d}^\dagger \hat{c}_i \frac{1}{\omega - \hat{H}_0} \hat{c}_j^\dagger \hat{d} \frac{1}{\omega - \hat{H}} \hat{d}^\dagger | 0 \rangle \\ &= G_0(\omega) + \sum_{ij} t_{io} t_{jo} G_0(\omega) G_{ij}^{(o)} G(\omega), \end{aligned} \quad (4.48)$$

note that here  $G_0$  and  $G$  are Green's functions of the impurity and  $G_{ij}^{(o)}$  is the Green's function of the lattice with site  $o$  removed. The above expression can be written in another form as

$$G^{-1}(\omega) = G_0^{-1}(\omega) - \sum_{ij} t_{io} t_{jo} G_{ij}^{(o)}. \quad (4.49)$$

For a general lattice we have

$$G^{(o)} = G_{ij} - \frac{G_{io} G_{oj}}{G_{oo}}, \quad (4.50)$$

therefore (4.49) becomes

$$G^{-1} = G_0^{-1} - \sum_{ij} t_{io} t_{jo} G_{ij} + \frac{(\sum_i G_{oi})}{G_{oo}}. \quad (4.51)$$

The summation over site  $i, j$  can be transformed into  $k$  space and we obtain that

$$G^{-1} = G_0^{-1} - \int d\varepsilon \frac{\rho(\varepsilon)\varepsilon^2}{\zeta - \varepsilon} - \left( \int d\varepsilon \frac{\rho(\varepsilon)\varepsilon}{\zeta - \varepsilon} \right) / \int d\varepsilon \frac{\rho(\varepsilon)}{\zeta - \varepsilon}, \quad (4.52)$$

where  $\zeta = \omega - \Sigma(\omega)$ . This can be simplified further using the following relations:

$$\int d\varepsilon \frac{\rho(\varepsilon)\varepsilon^2}{\zeta - \varepsilon} = \zeta \int d\varepsilon \frac{\rho(\varepsilon)\varepsilon}{\zeta - \varepsilon}, \quad \int d\varepsilon \frac{\rho(\varepsilon)}{\zeta - \varepsilon} = -1 + \zeta \int d\varepsilon \frac{\rho(\varepsilon)}{\zeta - \varepsilon}, \quad (4.53)$$

here we have used  $t_{oo} = \sum_k t_k = \int \rho(\varepsilon)\varepsilon = 0$ . Finally the required equation is obtained that

$$G_0^{-1} = \Sigma + G^{-1}. \quad (4.54)$$

## Chapter 5

# Strong Electron-Phonon Interaction and Colossal Magnetoresistance in $\text{EuTiO}_3$

In this chapter we shall apply the technique described in the previous chapters to investigate the electron transport properties in a real material:  $\text{EuTiO}_3$ . Especially, we shall explain the colossal magnetoresistance phenomenon in  $\text{EuTiO}_3$  by a dynamical mean-field theory.  $\text{EuTiO}_3$  is magnetic material, its magnetization rises as magnetic field increases and temperature decreases. Its Néel temperature is about 5.4 K. At around 15 K,  $\text{EuTiO}_3$  also exhibits colossal magnetoresistance: in the presence of magnetic field its resistivity drops dramatically.

### 5.1 Magnetoresistance

Before go to colossal magnetoresistance, we need to first know what is magnetoresistance. The concept is simple: the electrical resistivity of the material changes in the presence of an external magnetic field, such phenomenon is called magnetoresistance effect. The first ordinary magnetoresistance effect was discovered by William Thomson (Lord Kelvin) in 1856 [97].

## Giant Magnetoresistance

The resistivity change in ordinary magnetoresistance is small. In 1988 giant magnetoresistance was discovered by Mario Baibich *et al.* [98]. At the same time G. Binasch *et al.* also discovered giant magnetoresistance independently [99]. The resistivity can change up to 50% which is much larger than ordinary magnetoresistance effect. The giant magnetoresistance effect is widely used in computer industry. A typical example is the hard disk we use everyday. The giant magnetoresistance is so important that Albert Fert [98] and Peter Gruber [99] shared the 2007 Nobel Prize in Physics for the discovery of giant magnetoresistance.

## Colossal Magnetoresistance

Colossal magnetoresistance was first discovered in mixed-valence manganites in the 1950s by G. H. Jonker and J. H. van Santen [100]. In the 1990s colossal magnetoresistance was discovered in  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{A} = \text{Ca}, \text{Sr}$ ) by S. Jin *et al.* [101]. The term “colossal” arise from the huge change of the resistivity, if normalized to zero field values the resistivity changes up to 99.9%.

A first theoretical description for colossal magnetoresistance is based on *double exchange* mechanism. However, Andrew Millis *et al.* pointed out that double exchange alone is not enough to explain the colossal magnetoresistance in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  [3]. Later they explained the colossal magnetoresistance by double exchange mechanism and strong electron-phonon interaction [4].

Here we give a brief introduction on double exchange mechanism in order to get an quick view on the colossal magnetoresistance in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ .

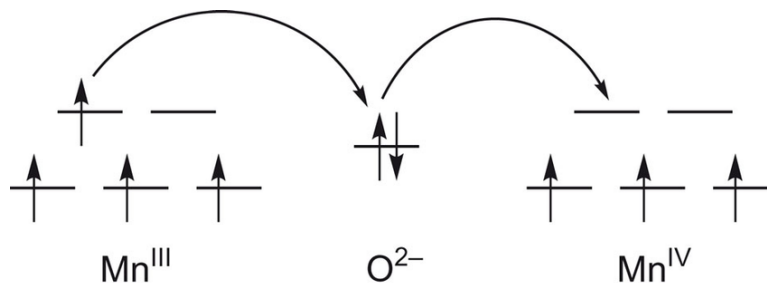


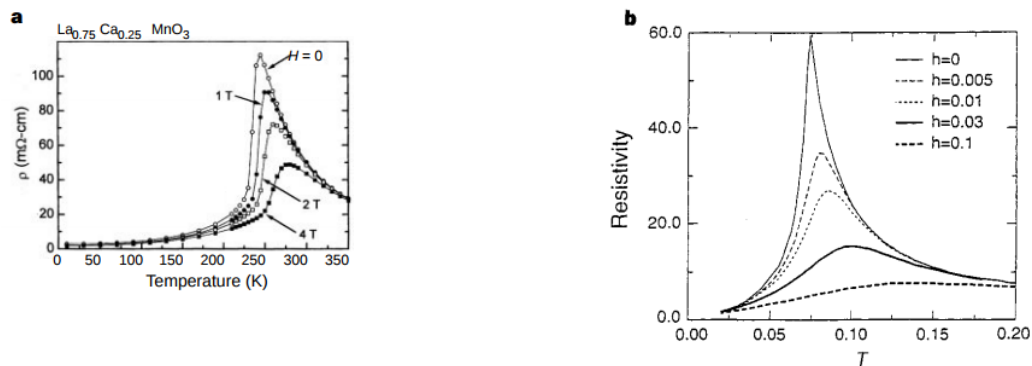
Figure 5.1: Schematic diagram for double exchange mechanism.

In  $\text{LaMnO}_3$  electrons fill the  $3d$  shell of the Mn ions, see left side of Figure 5.1. When doped with Sr, there would be  $4 - x$  electrons, or  $x$  holes, in the  $3d$  shell of the Mn ions. These holes (or

electrons) can hop from a Mn ion to another through oxygen ions, but due to strong Hund coupling this hopping process is inhibited if the ionic spins of the Mn are antiparallel. In other words, hopping is dependent on the relative orientation of the ionic spins. Such mechanism is called “double exchange” which was first proposed by Clarence Zener [12]. The effective Hamiltonian presenting double exchange mechanism is usually written in the form of the Hamiltonian of Kondo model [13, 14].

In the system features double exchange mechanism, there would be strong exchange interaction between itinerant electrons and Mn ionic spins. This would cause strong spin scatterings for itinerant electrons.

The calculated resistivity done by Millis *et al.* is shown in Figure 5.2. Here we quote the



**Figure 3** Measured and calculated resistivity of  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ . **a**, Measured resistivity at different magnetic fields: from ref. 7. **b**, Calculated resistivity (arbitrary unites) versus temperature  $T$  in different magnetic fields  $h$ , from ref. 16.  $h = 0.01$

corresponds to a field of 6 T.  $T = 0.1$  corresponds to a temperature of 1/40 of the bandwidth used in the calculation.

Figure 5.2: A. J. Millis, Nature, **392**, 147 (1998)

explanation from the work of Millis *et al.* as the explanation of the colossal magnetoresistance of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ :

At small  $\lambda$  and  $T > T_c$ ,  $\rho$  is small and has a  $T$ -independent piece due to the spin disorder and a  $T$ -linear piece due to electron-phonon scattering. As  $T$  is decreased through  $T_c$ ,  $\rho$  drops as the spin scattering is frozen out and the phonon contribution changes slightly. For larger  $\lambda$  a gap opens in the electron spectral function at  $T > T_c$  and  $\rho$  rises as  $T$  is lowered to  $T_c$ . Below  $T_c$ ,  $\rho$  drops sharply as the gap closes and metallic behavior is restored.

A. J. Millis *et al.* [4]

It is clear from the description above that there exists a phase transition for spins and different

phases of spins would affect the transport properties of electrons greatly. Therefore the transition temperature of spins  $T_c$  has significant effects on the turning point of resistivity.

## 5.2 Magnetization of $\text{EuTiO}_3$

In this section we shall calculate the magnetization of  $\text{EuTiO}_3$ , which is closely related to the colossal magnetoresistance, by usual Weiss mean-field theory. It is shown that Weiss mean-field theory calculation fits the experimental data quite well [102–105], thus we shall just use mean-field results instead of experimental ones for magnetization data.

The ions  $\text{Eu}^{2+}(4f^7)$  in  $\text{EuTiO}_3$  have a large localized spin ( $S = 7/2$ ), which is the source of magnetism. The magnetic properties of  $\text{EuTiO}_3$  can be described by a Heisenberg model with the Hamiltonian [106]

$$\hat{H} = -J_1 \sum_{\langle ij \rangle} \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j - J_2 \sum_{[ij]} \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j - g\mu_B \mathbf{B} \cdot \sum_i \hat{\mathbf{s}}_i, \quad (5.1)$$

where  $\langle ij \rangle$  denotes the summation over nearest neighbors and  $[ij]$  denotes the summation over next nearest neighbors. The values of the parameters are

$$J_1 = -0.037 k_B \text{K}, \quad J_2 = 0.069 k_B \text{K}, \quad (5.2)$$

and with such values the Néel temperature of  $\text{EuTiO}_3$  is about 5.4 K. The Landé factor  $g$  is 2 and  $\mu_B$  is the Bohr magneton.

In order to apply mean-field theory for an anti-ferromagnetic system, we need to separate the lattice into two sublattices and label them as  $a$  lattice and  $b$  lattice, see Figure 5.3.

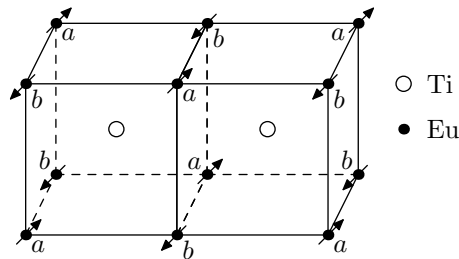


Figure 5.3: The localized spin model for  $\text{EuTiO}_3$ .

It can be seen that the nearest neighbors of sites  $a$  are sites  $b$ , and the next nearest neighbors of



sites  $a$  are sites  $a$  again, vice versa for sites  $b$ . Accordingly, the Hamiltonian (5.1) can be separated into two parts:

$$\hat{H} = \hat{H}_a + \hat{H}_b, \quad (5.3)$$

where

$$\hat{H}_a = -\mathbf{F}_a \cdot \hat{\mathbf{s}}_a, \quad \hat{H}_b = -\mathbf{F}_b \cdot \hat{\mathbf{s}}_b. \quad (5.4)$$

Here  $\mathbf{F}_a$  and  $\mathbf{F}_b$  are the effective fields for sites  $a$  and  $b$  respectively, and they are related to the average spins by formula

$$\mathbf{F}_a = 6J_1\langle\hat{\mathbf{s}}_b\rangle + 12J_2\langle\hat{\mathbf{s}}_b\rangle + g\mu\mathbf{B}, \quad \mathbf{F}_b = 6J_1\langle\hat{\mathbf{s}}_a\rangle + 12J_2\langle\hat{\mathbf{s}}_a\rangle + g\mu\mathbf{B}, \quad (5.5)$$

where the factor 6 and 12 are the numbers of nearest and next nearest neighbors. The equation (5.4) then can be written in a component form as

$$\hat{H}_a = -F_a^x \hat{s}_a^x - F_a^y \hat{s}_a^y - F_a^z \hat{s}_a^z, \quad \hat{H}_b = -F_b^x \hat{s}_b^x - F_b^y \hat{s}_b^y - F_b^z \hat{s}_b^z. \quad (5.6)$$

From standard quantum mechanics we know the matrix elements for spin operators are just

$$\begin{aligned} \langle\sigma|\hat{s}_x|\sigma-1\rangle &= \langle\sigma-1|\hat{s}_x|\sigma\rangle = \frac{1}{2}\sqrt{(S+\sigma)(S-\sigma+1)}; \\ \langle\sigma|\hat{s}_y|\sigma-1\rangle &= -\langle\sigma-1|\hat{s}_y|\sigma\rangle = -\frac{i}{2}\sqrt{(S+\sigma)(S-\sigma+1)}; \\ \langle\sigma|\hat{s}_z|\sigma\rangle &= \sigma, \end{aligned} \quad (5.7)$$

where  $\sigma$  is the spin index.

Now suppose the Hamiltonian is already diagonalized and let  $E_n$  denote the eigenvalue and  $|n\rangle$  denote the corresponding eigenvector, then the canonical distribution probability can be written as

$$\rho_n = \frac{1}{Z} e^{-\frac{E_n}{T}}, \quad (5.8)$$

where  $Z$  is the partition function. Thus the average localized spin is just

$$\langle\hat{\mathbf{s}}\rangle = \sum_n \rho_n \langle n|\hat{\mathbf{s}}|n\rangle, \quad (5.9)$$

or in component form

$$\langle \hat{s}_x \rangle = \sum_n \rho_n \langle n | \hat{s}_x | n \rangle, \quad \langle \hat{s}_y \rangle = \sum_n \rho_n \langle n | \hat{s}_y | n \rangle, \quad \langle \hat{s}_z \rangle = \sum_n \rho_n \langle n | \hat{s}_z | n \rangle. \quad (5.10)$$

Equations (5.5) and (5.9) together form a system of self-consistent equations, and we can find the numerical solutions by iteration. Finally we obtain the magnetization as

$$\mathbf{M} = g\mu_B \frac{\langle \hat{s}_a + \hat{s}_b \rangle}{2}. \quad (5.11)$$

Since the Landé factor is 2 here and for latter calculation, it is convenient to define the magnetization as a dimensionless quantity as

$$\mathbf{M} = \langle \hat{s} \rangle = \frac{1}{2} \langle \hat{s}_a + \hat{s}_b \rangle. \quad (5.12)$$

The results of mean-field calculation for  $M = |\mathbf{M}|$  are shown in Figure 5.4.

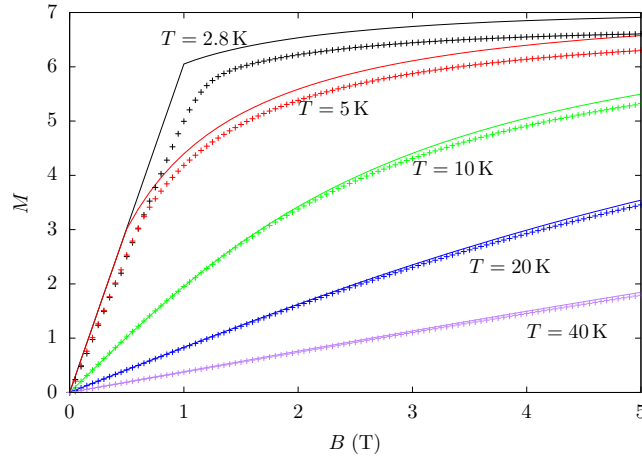


Figure 5.4: Experimental data (dots) and Mean-Field calculation (solid lines) of magnetization for  $\text{EuTiO}_3$  with different temperature and magnetic field. The experimental data are provided by Km Rubi and Prof. Mahendiran.

The above formulas can be simplified considering the rotation symmetry of the spins. Let us define the direction of magnetic field  $\mathbf{B}$  as the  $z$ -axis, then a localized spin has a rotation symmetry with respect to  $z$ -axis. In other words, any vector in the  $xy$  plane can be rotated to the  $x$ -axis and the equation (5.6) can be then reduced to

$$\hat{H}_a = -F_a^x \hat{s}_a^x - F_a^z \hat{s}_a^z, \quad \hat{H}_b = -F_b^x \hat{s}_b^x - F_b^z \hat{s}_b^z, \quad (5.13)$$

with (here  $B = |\mathbf{B}|$ )

$$\begin{cases} F_a^x = 6J_1\langle\hat{s}_b^x\rangle + 12J_2\langle\hat{s}_a^x\rangle, & F_a^z = 6J_1\langle\hat{s}_b^z\rangle + 12J_2\langle\hat{s}_a^z\rangle + g\mu B; \\ F_b^x = 6J_1\langle\hat{s}_a^x\rangle + 12J_2\langle\hat{s}_b^x\rangle, & F_b^z = 6J_1\langle\hat{s}_a^z\rangle + 12J_2\langle\hat{s}_b^z\rangle + g\mu B. \end{cases} \quad (5.14)$$

According to (5.4) the Hamiltonian for spin can be written as  $\hat{H} = -\mathbf{F} \cdot \hat{\mathbf{s}}$ . Note that  $\mathbf{F}$  is a vector with length  $\sqrt{F_x^2 + F_z^2}$  and the inner product  $\mathbf{F} \cdot \hat{\mathbf{s}}$  is an invariant quantity under rotation, thus we can take the direction of  $\mathbf{F}$  as the  $z$ -axis for the moment. Then the canonical distribution probability and the partition function becomes

$$\rho_\sigma = \frac{1}{Z} \exp\left(\frac{\sqrt{F_x^2 + F_z^2}}{T}\sigma\right), \quad Z = \sum_\sigma \exp\left(\frac{\sqrt{F_x^2 + F_z^2}}{T}\sigma\right), \quad (5.15)$$

where  $\sigma = -7/2, -5/2, \dots, 5/2, 7/2$  is the spin index. Let  $\chi$  denote  $\sqrt{F_x^2 + F_z^2}/T$ , then the average spin in the direction of  $\mathbf{F}$  is

$$\begin{aligned} \sum_\sigma \sigma \rho_\sigma &= \left(\sum_\sigma \sigma e^{\chi\sigma}\right) \left(\sum_\sigma e^{\chi\sigma}\right)^{-1} \\ &= \frac{d}{d\chi} \ln \sum_\sigma e^{\chi\sigma} \\ &= \frac{d}{d\chi} \ln \left[ \frac{e^{-\frac{7}{2}\chi} - e^{\frac{9}{2}\chi}}{1 - e^\chi} \right] \\ &= \left( -\frac{7}{2}e^{-\frac{7}{2}\chi} - \frac{9}{2}e^{\frac{9}{2}\chi} + e^\chi \frac{e^{-\frac{7}{2}\chi} - e^{\frac{9}{2}\chi}}{1 - e^\chi} \right) \left( e^{-\frac{7}{2}\chi} - e^{\frac{9}{2}\chi} \right)^{-1} \\ &= \left( -4e^{-\frac{7}{2}\chi} - 4e^{\frac{9}{2}\chi} + \frac{1}{2}e^{-\frac{7}{2}\chi} - \frac{1}{2}e^{\frac{9}{2}\chi} + e^\chi \frac{e^{-\frac{7}{2}\chi} - e^{\frac{9}{2}\chi}}{1 - e^\chi} \right) \left( e^{-\frac{7}{2}\chi} - e^{\frac{9}{2}\chi} \right)^{-1} \\ &= 4 \frac{e^{4\chi} + e^{-4\chi}}{e^{4\chi} - e^{-4\chi}} - \frac{1}{2} \frac{e^{\frac{1}{2}\chi} + e^{-\frac{1}{2}\chi}}{e^{\frac{1}{2}\chi} - e^{-\frac{1}{2}\chi}} \\ &= 4 \coth 4\chi - \frac{1}{2} \coth \frac{1}{2}\chi \\ &= \frac{7}{2} B_{\frac{7}{2}}\left(\frac{7}{2}\chi\right), \end{aligned} \quad (5.16)$$

where  $B_J(x)$  is the *Brillouin function* which is defined as

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}x\right). \quad (5.17)$$

Let us return to normal  $x - z$  plane, the components of the average spin in  $x, z$  directions can be then written as

$$\langle \hat{s}_x \rangle = \frac{\frac{7}{2} F_x B_{\frac{7}{2}} (\frac{7}{2} \chi)}{\sqrt{F_x^2 + F_z^2}}, \quad \langle \hat{s}_z \rangle = \frac{\frac{7}{2} F_z B_{\frac{7}{2}} (\frac{7}{2} \chi)}{\sqrt{F_x^2 + F_z^2}}. \quad (5.18)$$

We can write the above formulas for different sublattices explicitly as

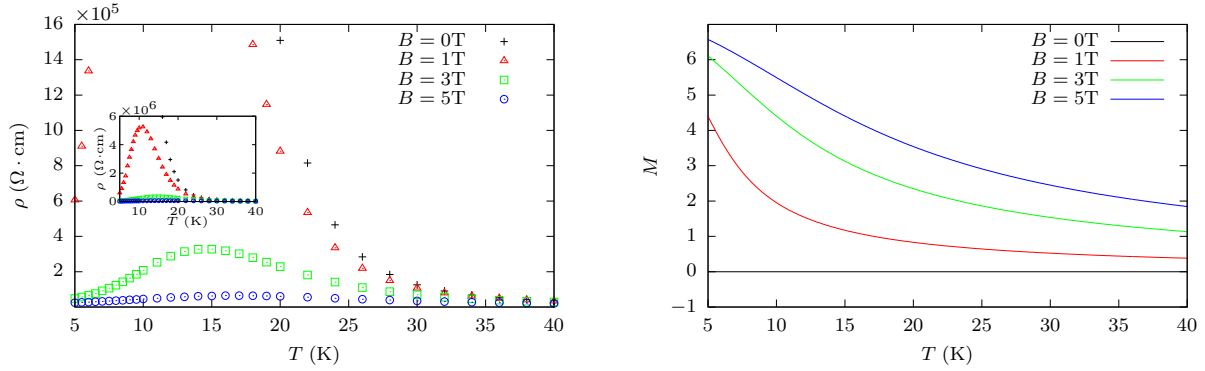
$$\begin{aligned} \langle \hat{s}_a^x \rangle &= \frac{\frac{7}{2} F_a^x B_{\frac{7}{2}} (\frac{7}{2} \chi_a)}{\sqrt{(F_a^x)^2 + (F_a^z)^2}}, & \langle \hat{s}_a^z \rangle &= \frac{\frac{7}{2} F_a^z B_{\frac{7}{2}} (\frac{7}{2} \chi_a)}{\sqrt{(F_a^x)^2 + (F_a^z)^2}}, \\ \langle \hat{s}_b^x \rangle &= \frac{\frac{7}{2} F_b^x B_{\frac{7}{2}} (\frac{7}{2} \chi_b)}{\sqrt{(F_b^x)^2 + (F_b^z)^2}}, & \langle \hat{s}_b^z \rangle &= \frac{\frac{7}{2} F_b^z B_{\frac{7}{2}} (\frac{7}{2} \chi_b)}{\sqrt{(F_b^x)^2 + (F_b^z)^2}}. \end{aligned} \quad (5.19)$$

### 5.3 Colossal Magnetoresistance in $\text{EuTiO}_3$

The colossal magnetoresistance observed in manganites (doped  $\text{R}_{1-x}\text{A}_x\text{MnO}_3$  oxides, where R and A are a trivalent rare earth) has attracted much attention for the past two decades [3–11], both for its possible utility in technology and a better theoretical understanding of magnetoresistance. Reports on magnetoresistance in rare earth titanates of formula  $\text{RTiO}_3$  are scarce due to their large resistivities at low temperature. Recently Km Rubi *et al.* [15, 16] found that the undoped perovskite titanium oxide  $\text{EuTiO}_3$  exhibits colossal magnetoresistance below 40 K [15]. In the experiments, polycrystalline  $\text{EuTiO}_3$  sample was prepared using a standard solid state reaction method in reduced atmosphere (95% Ar and 5%  $\text{H}_2$ ). More details about the sample preparation can be found in references [16, 105]. The DC resistivity was measured in a Physical Property Measurement System using an electrometer in two probe configuration. The experimental resistivities and the corresponding magnetization are shown in Fig 5.5.

It can be seen that resistivities are quite high: most resistivities are larger than  $10^5 \Omega \cdot \text{cm}$ . Such values of resistivity can almost compare to the values of an insulator. When an external magnetic field is present, the resistivity drops dramatically. The resistivity changes more dramatically when the magnetic field is larger, and larger magnetic field means larger magnetization. This reminds us that the change of resistivity may relate to the change of magnetization.

Here we should notice the differences between colossal magnetoresistance in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  and  $\text{EuTiO}_3$ . It can be seen from Figure 5.2 that even without external magnetic field when



(a) Experimental resistivities with different temperature and magnetic field. The inset represents the same data but with a larger scale. The data are provided by Km Rubi and Prof. Mahendiran.

(b) Mean-field calculation of magnetization, where  $M = |\mathbf{M}|$  is defined to a dimensionless quantity.

Figure 5.5: Experimental resistivities and mean-field calculation of magnetization of  $\text{EuTiO}_3$ .

temperature is decreased through some  $T_c$  the resistivity of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  drops. But without external magnetic field the resistivity of  $\text{EuTiO}_3$  (see Figure 5.5(a)) always increases as temperature decreases.  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  is essentially a metallic system, this is the reason it owns such a resistivity behavior. Considering the high resistivity and the resistivity behavior without magnetic field of  $\text{EuTiO}_3$ , this indicates that  $\text{EuTiO}_3$  is essentially an insulator or semiconductor. According to the description of Millis *et al.*, the  $T_c$  of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  is related to the phase transition point of spins. However, we already know that the transition temperature (Néel temperature) of  $\text{EuTiO}_3$  is about 5.4K while the turning point of resistivity is about 15 K. This indicates that the colossal magnetoresistance in  $\text{EuTiO}_3$  may be irrelevant with spin phase transition.

### Simple Fitting

Based on these observations, we first try a simple model to fit the experimental data. The schematic depiction of the model is shown in Fig 5.6. We assume the conduction electrons hop between different Ti atoms and form a tight-binding model. The localized spins on  $\text{Eu}^{2+}$ , as we mentioned earlier, are described by a Heisenberg model, and the interaction between conduction electrons and localized spins is assumed to be a simple exchange interaction [107]. Therefore, we write the

Hamiltonian for conduction electrons as

$$\hat{H} = \hat{H}_0 + \hat{H}_1, \quad (5.20)$$

with

$$\hat{H}_0 = - \sum_{ij,\alpha} t_{ij} \hat{c}_{i\alpha}^\dagger \hat{c}_{j\alpha}, \quad \hat{H}_1 = J \sum_i \hat{\mathbf{s}}_i \cdot \mathbf{M}(T, B), \quad (5.21)$$

where  $\hat{c}_{i\alpha}^\dagger$  ( $\hat{c}_{i\alpha}$ ) creates (destroys) an electron with spin  $\alpha$  at site  $i$ ,  $J$  is the exchange coupling strength and  $\hat{\mathbf{s}}_i = \sum_{\alpha\beta} \hat{c}_{i\alpha} \boldsymbol{\sigma}_{\alpha\beta} \hat{c}_{i\beta}$  is the electron spin operator at site  $i$  with  $\boldsymbol{\sigma}_{\alpha\beta}$ . Here  $\boldsymbol{\sigma}_{\alpha\beta}$  is the Pauli matrices vector and  $\mathbf{M}(T, B)$  is the magnetization of the material which, according to the previous section, is a function of temperature and magnetic field.

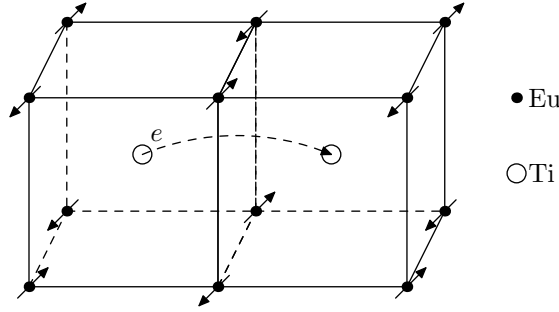


Figure 5.6: Schematic depiction of the  $\text{EuTiO}_3$  model

For simplicity, we shall apply Einstein's formula introduced in section 2.1 to calculate the conductivity:

$$\sigma = neb, \quad b = \frac{eD}{T}, \quad (5.22)$$

where  $D$  is the diffusion constant and  $b$  is the electrical mobility. The term  $\hat{H}_0$  is just the Hamiltonian of a cubic tight-binding model which can be solved exactly and the resulting dispersion relation is well known as

$$\varepsilon_{\mathbf{k}} = -2t[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)], \quad (5.23)$$

where  $a$  is the lattice constant. For  $\text{EuTiO}_3$ , the lattice constant is about  $4 \text{ \AA} = 4 \times 10^{-8} \text{ cm}$  [106, 108, 109]. The behavior of the resistivity of  $\text{EuTiO}_3$  indicates it is semiconductor, i.e., the position of the chemical potential is below the band bottom. Therefore we can expand the dispersion

up to second order and obtain

$$\varepsilon_{\mathbf{k}} = -6t + ta^2k^2, \quad (5.24)$$

where  $k = |\mathbf{k}|$ . Here  $-6t$  is the position of the band bottom. Since the chemical potential is below the band bottom the electrons obey a Boltzmann distribution  $f(\varepsilon) = \exp[(\mu - \varepsilon)/T]$ , and the carrier density is then

$$\begin{aligned} n &= 2 \int e^{(\mu - \varepsilon_{\mathbf{k}})/T} \frac{dk^3}{(2\pi)^3} \\ &= \frac{2}{(2\pi)^3} \int k^2 e^{(\mu + 6t - ta^2k^2)/T} \sin\theta d\theta d\phi dk \\ &= \frac{2}{2\pi^2} \int k^2 e^{(\mu + 6t - ta^2k^2)/T} dk \\ &= 2 \left( \frac{T}{2\pi ta^2} \right)^{\frac{3}{2}} e^{-\Delta E/T}, \end{aligned} \quad (5.25)$$

where the factor 2 is the electron spin degeneracy,  $\Delta E = -6t - \mu$  is the gap between band bottom and the chemical potential. In the above integration we have used the formulas of transformation from Cartesian coordinates to spherical coordinates. With this carrier density, the conductivity is simply

$$\sigma = 2 \frac{e^2 D}{T} \left( \frac{T}{2\pi ta^2} \right)^{\frac{3}{2}} e^{-\Delta E/T}. \quad (5.26)$$

From the above formula it can be seen that the value of  $\Delta E$  is of fundamental importance since it dominates the conductivity. Thus we shall first try to extract the value of  $\Delta E$  from experimental data. Since the exponential factor dominates, the formula of conductivity may be approximately written as

$$\sigma \approx \text{constant} \times e^{-\Delta E/T}, \quad (5.27)$$

and fitting it to the experimental resistivity without magnetic field yields, see Figure 5.7,  $\Delta E \approx 153 k_B K \approx 0.013 \text{ eV}$ . It should be noted that such value of  $\Delta E$  is fairly small for such large resistivities of  $\text{EuTiO}_3$ . And with this value of  $\Delta E$  the typical values of carrier density are, suppose  $t = 0.1 \text{ eV} \approx 1160 k_B K^1$ ,

$$n(T = 40 \text{ K}) \approx 9.8 \times 10^{16} \text{ cm}^{-3}, \quad n(T = 300 \text{ K}) \approx 5.54 \times 10^{19} \text{ cm}^{-3}. \quad (5.28)$$

---

<sup>1</sup>This value of  $t$  corresponds to a conduction band with bandwidth 1.2 eV, which is a rather narrow conduction band.

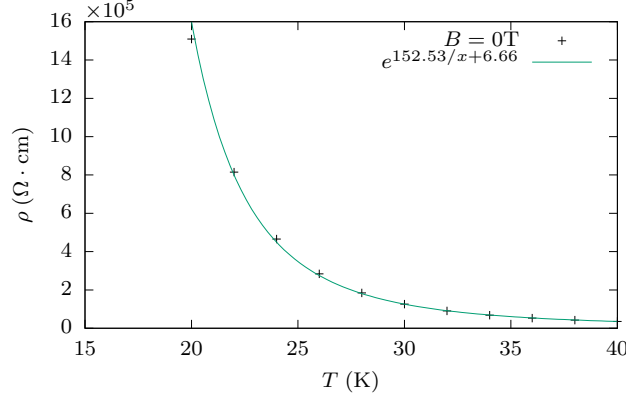


Figure 5.7: Resistivity without magnetic field. A function  $y = e^{152.53/x+6.66}$  is used to fit the experimental resistivity, where  $y = \rho/(\Omega \cdot \text{cm})$  and  $x = T/\text{K}$ .

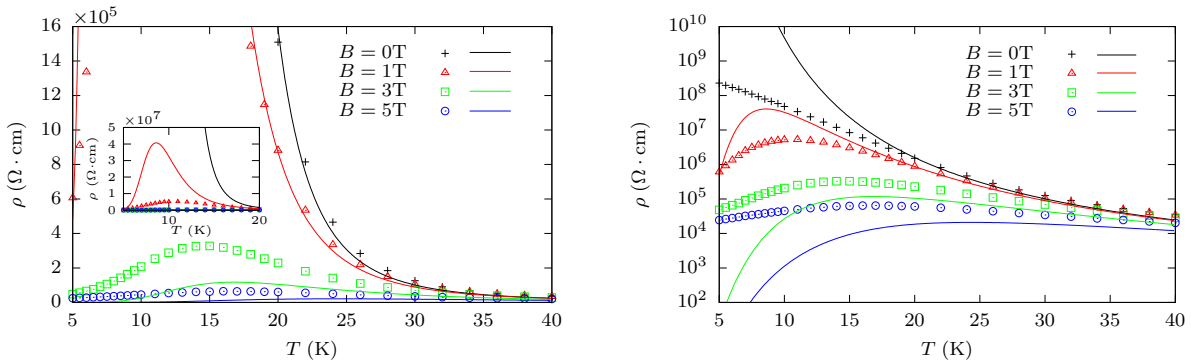
Now let us return to  $\hat{H}_1$ . It is easy to see that  $\hat{H}_1$  just shifts the energy band by  $\pm \frac{1}{2}JM$  for spin up and down. With this shifting, the carrier density becomes

$$n = \left( \frac{T}{2\pi t a^2} \right)^{\frac{3}{2}} \left[ \exp \left( -\frac{\Delta E - \frac{1}{2}JM}{T} \right) + \exp \left( -\frac{\Delta E + \frac{1}{2}JM}{T} \right) \right], \quad (5.29)$$

and the conductivity accordingly becomes

$$\sigma = \frac{e^2 D}{T} \left( \frac{T}{2\pi t a^2} \right)^{\frac{3}{2}} \left[ \exp \left( -\frac{\Delta E - \frac{1}{2}JM}{T} \right) + \exp \left( -\frac{\Delta E + \frac{1}{2}JM}{T} \right) \right]. \quad (5.30)$$

For simplicity, we assume the diffusion constant is a constant at different temperature. Let  $D = 9 \times 10^{-6} \text{ cm}^2/\text{s}$  and  $J = 0.005 \text{ eV}$ , and we shall get fitting results shown in Figure 5.8.



(a) Resistivities with normal scale, here the inset represents the same data but with a larger scale.

(b) Resistivities with logarithmic scale.

Figure 5.8: Simple fitting resistivities (lines), and the experimental data (dots) are plotted here for comparison.



It can be seen from the figure that this simple fitting, although the result with  $B = 1 \text{ T}$  is not good, indeed reflects the essential part of colossal magnetoresistance. From this point we can say that the band shift caused by magnetization of the material plays a fundamental rule in colossal magnetoresistance in  $\text{EuTiO}_3$ . However, here is a significant flaw in this fitting: the value of diffusion constant  $D$  is too small.

This simple fitting can not explain such a small diffusion constant. If a diffusion constant with normal value is desired then we need a much smaller carrier density. The gap  $\Delta E$  is already determined by experimental data, the only thing we can do to reduce the carrier density is to decrease the bandwidth of the conduction band. But the conduction band we use now (with bandwidth  $12t = 1.2 \text{ eV}$ ) is already a narrow band, if we decrease the bandwidth further then the electrons would be considered as localized electrons, not conduction electrons. This contradiction indicates that some other factors need to be taken into consideration rather than applying the theory of semiconductors directly as in this simple fitting.

## 5.4 Strong Electron-Phonon Interaction in $\text{EuTiO}_3$

In the 1990s, several works show that in manganites the strong electron-phonon interaction plays an important role in colossal magnetoresistance [3–11]. Andrew Millis first pointed out that double-exchange mechanism is not enough to explain the colossal magnetoresistance in manganites and Jahn-Teller effects must be taken into consideration:

Double Exchange Alone Does Not Explain the Resistivity of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

.....

We present a solution of the double-exchange model, show it is incompatible with many aspects of the data, and propose that in addition to double-exchange physics a strong electron-phonon interaction arising from the Jahn-Teller splitting of the outer Mn  $d$  level plays a crucial role.

A. J. Millis *et al* [3]

The interplay of these two effects (Jahn-Teller and double exchange) as the electron phonon coupling is varied reproduces the observed behavior of the resistivity and magnetic transition temperature.

A. J. Millis *et al* [4]

The strong Jahn-Teller effect would lead to a polaronic effect, therefore Millis wrote

The novelty of the manganites is the occurrence of self-trapping at a high density of electrons.

A. J. Millis [6]

Jun Zang also showed that Jahn-Teller effect contributes to the magnetoresistance in manganites:

We also found that JT distortion fluctuations will contribute to magnetoresistance at moderate and high temperatures, especially concerning its T dependence.

J. Zang *et al* [7]

Later Guo-Meng Zhao showed that the resistivity behavior in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  is consistent with small polaron coherent motion:

We report measurements of the resistivity in the ferromagnetic state of epitaxial thin films of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  . . . . Such behavior is consistent with small-polaron coherent motion which involves a relaxation due to a soft optical phonon mode that is strongly coupled to the carriers.

G.-M. Zhao *et al* [11]

From the above quotations, it is clear that strong electron-phonon interaction indeed plays a fundamental role in the colossal magnetoresistance of manganites. So, here comes a question: is the electron-phonon interaction also important for the colossal magnetoresistance in  $\text{EuTiO}_3$ ? Despite the quotations above, we have another reason to believe there also exists strong electron-phonon interaction in  $\text{EuTiO}_3$ : the small polaron effect has been observed in a titanium oxide, rutile ( $\text{TiO}_2$ ), single crystal by Vladislav Bogomolov [110, 111]. The observed transition temperature from small polaron coherent motion to thermal activated motion of rutile is about  $300^\circ\text{C}$ , this is also mentioned in Gerald Mahan's book:

There have been many experimental systems with these characteristics which have been ascribed to small-polaron theory. One example is  $\text{TiO}_2$  (Bogomolov). They observe the transition from band to hopping conductivity at about  $300^\circ\text{C}$ .

G. D. Mahan [112]

In view of the above mentioned reasons, we shall also take strong electron-phonon interaction into consideration for colossal magnetoresistance in  $\text{EuTiO}_3$  and use small polaron to model it.

## 5.5 Strong Electron-Phonon Interaction and Colossal Magnetoresistance in $\text{EuTiO}_3$

According to discussions in previous sections, we decided to take strong electron-phonon interaction into consideration and use a small polaron formalism to model it in  $\text{EuTiO}_3$  [15]. Therefore we replace  $\hat{H}_0$  in (5.20) by a Holstein model Hamiltonian [94, 95]:

$$\hat{H}_0 = - \sum_{ij,\alpha} t_{ij} \hat{c}_{i\alpha}^\dagger \hat{c}_{j\alpha} + \omega_0 \sum_i \hat{a}_i^\dagger \hat{a}_i + g \sum_{i\alpha} \hat{c}_{i\alpha}^\dagger \hat{c}_{i\alpha} (\hat{a}_i + \hat{a}_i^\dagger). \quad (5.31)$$

The operator  $\hat{c}_{i\alpha}^\dagger$  ( $\hat{c}_{i\alpha}$ ) creates (destroys) an electron with spin  $\alpha$  at site  $i$ , while  $\hat{a}_i^\dagger$  ( $\hat{a}_{i\alpha}$ ) creates (destroys) a dispersionless optical phonon at site  $i$ . The frequency of the optical phonon is denoted by  $\omega_0$  and the coupling strength of the electron-phonon interaction is denoted by  $g$ . The term  $\hat{H}_1$  remains the same as (5.20), which would just shift the energy band obtained via  $\hat{H}_0$ .

Back to (5.27), it should be emphasized that although the thermally activated hopping process of small polaron gives the same form of conductivity [92, 93], (5.27) is unlikely due to this process. This can be argued as follows. The hopping process begins to dominate when temperature is above a transition temperature which is about  $0.4\omega_0$  [92, 93, 112]. However, according to first principle calculations, the highest frequency of optical phonons is about 0.1 eV [113], and we assume it to be the value of  $\omega_0$ . This value means that the transition temperature is about 464 K, which is far above 40 K. Besides, experiments showed that the transition temperature of rutile ( $\text{TiO}_2$ ) is about 300 K [110–112], which is also far above 40 K.

Here we shall apply the dynamical mean-field theory for small polaron at zero temperature<sup>2</sup>

---

<sup>2</sup>The temperature here is low enough to be treated as zero temperature when calculating the electronic structure.

discussed in the previous chapter to handle  $\hat{H}_0$ . To obtain the electronic structure of a specified material, the density of states given by a first principle calculation is needed. The conduction band of  $\text{EuTiO}_3$  consists of  $t_{2g}$  orbitals of Ti atom, and its density of states was calculated via density functional theory by Quantum Espresso [114] which is shown in Figure 5.9.

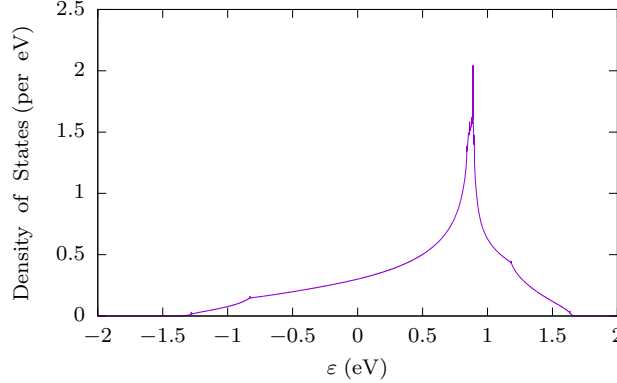


Figure 5.9: The density of states of  $t_{2g}$  orbitals of Ti atom by a first principle calculation. The Fermi level, which needs to be fitted by experimental data later, is not specified here. The first principle density functional theory calculation is carried out within the spin-polarized generalized gradient approximation (GGA) [115] using norm-conserving pseudopotentials. We use a kinetic energy cutoff of 60 Ry and a  $10 \times 10 \times 10$   $\Gamma$ -centered  $k$ -point mesh for the unit cell simulations. Then the mesh is interpolated up to  $40 \times 40 \times 40$  by Wannier functions [116, 117]. This calculation is done by Ji-Chang Ren.

After the dynamical mean-field theory calculation for  $\hat{H}_0$ , an energy dependent self-energy  $\Sigma_0(\varepsilon)$  and the corresponding retarded Green's function  $G_0(\varepsilon)$  are obtained, and the spectral density is then given by  $-\frac{1}{\pi}\text{Im}G_0(\varepsilon)$ . The spectral density calculated by dynamical mean-field theory with  $\hat{H}_0$  for different values of  $g$  is shown in Figure 5.10.

The spectral density with  $g < 0.6$  eV is nothing special, but when  $g$  increases to 0.6 eV a small peak appears at the bottom of the band, see Figure 5.10 (a). As  $g$  goes to 0.8 eV a second peak appears and the first one becomes lower, see Figure 5.10 (b). When  $g$  becomes larger, the second peak becomes much more obvious and the first becomes much smaller but still remains. It can be also seen in (d) that the main band starts to split into several subbands, these subbands are narrower than the original band, but they are still much broader than the first two peaks. In (f) the first peak is shifted outside the figure.

The first two peaks can be treated as two tiny subbands of the conduction band and they can

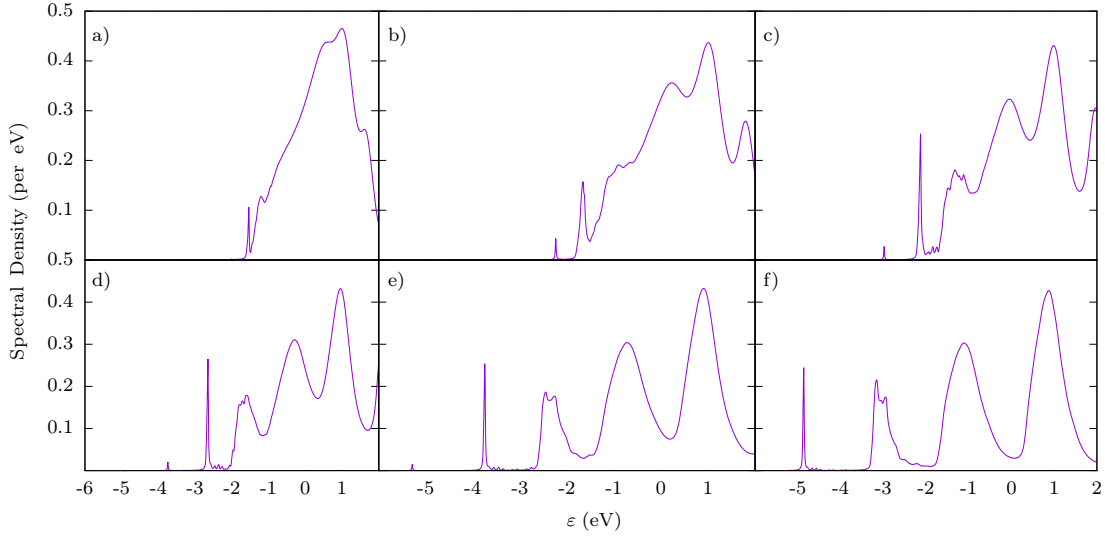


Figure 5.10: The spectral density calculated by dynamical mean-field theory with  $g =$  (a) 0.6 eV, (b) 0.8 eV, (c) 1.0 eV, (d) 1.2 eV, (e) 1.6 eV, and (f) 2.0 eV.

provide conduction electrons. At first glance, the first is too small and may be neglected. However, our calculation of resistivities shows that the second subband still provides too many electrons for such large resistivities of  $\text{EuTiO}_3$ . Thus we just focus on the first subband. If this subband is close to the Fermi level, then it can explain the smallness of  $\Delta E$ . And, since this subband is tiny, the carrier density would still be low, this can explain the high resistivities.

Now let us turn to the details of  $\hat{H}_1$ . The magnetization  $\mathbf{M}$  in  $\hat{H}_1$  is an average quantity, and writing  $\hat{H}_1$  in this form means that scattering due to localized spins is neglected. This is true only when the exchange coupling strength  $J$  is small. We shall see it is indeed this case later. The term  $\hat{H}_1$  would only shift the self-energy according to different spins of electrons, therefore the final self-energy is  $\Sigma_\alpha = \Sigma_0 \pm \frac{1}{2}JM(T, B)$  with  $M = |\mathbf{M}|$  for spin up and down respectively. And the final Green's function  $G_\alpha$  would change according to the self-energy shift for different spin, which is equivalent to the band shift for different spin.

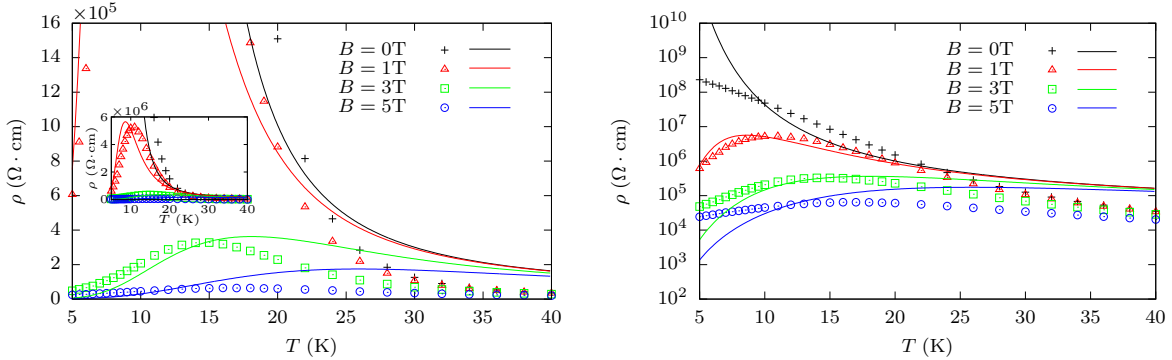
Instead of Einstein formula used in Simple fitting, the static conductivity can be calculated via the Kubo-Greenwood formula discussed in section 2.7:

$$\sigma = \frac{e^2 \hbar}{\pi V} \int \left( -\frac{\partial f}{\partial \varepsilon} \right) \text{Tr}[\hat{v}_x \text{Im}G(\varepsilon) \hat{v}_x \text{Im}G(\varepsilon)] d\varepsilon, \quad (5.32)$$

where  $V$  is the volume of system and  $\hat{v}_x$  is the operator for a component of velocity. Since the carrier

density is low, we can use Boltzmann's distribution  $f = \exp[(\mu - \varepsilon)/T]$ . Due to the band shift, the distribution function can be equivalently written as  $f = \exp[(\mu - \varepsilon \mp \frac{1}{2}JM)/T]$ . The band with spin down is shifted by  $-\frac{1}{2}JM$ , thus it goes closer to the Fermi level and provides more conduction electrons. While another band with spin up would be shifted away from the Fermi level and the carrier density in it would be reduced. However, because the distribution function is exponential, the total carrier density increases and the resistivity decreases accordingly. An important point here is that  $\Delta E$  is very small. Thus, even a small amount of shift, say  $30 k_B K \approx 0.0026 \text{ eV}$ , would cause an obvious difference, while in other materials such a small shift may be just ignored. This is the origin of colossal magnetoresistance in  $\text{EuTiO}_3$ .

Based on the first peak in figure 5.10 (c) with  $g = 1.0 \text{ eV}$  we have calculated resistivities of  $\text{EuTiO}_3$ . This value of  $g$ , of course, may not be accurate for the real situation, so we need to adjust our parameters to fit experimental data. We set the Fermi level at  $-3.0778 \text{ eV}$ . Note that, because the carrier density is very sensitive to the band shift, the position of the Fermi level needs to be carefully placed. The group velocity  $v_x(\mathbf{k})$  of electrons is obtained by our first principle calculation. The maximum velocity is about  $10^5 \text{ m/s}$ . The value of  $J$  is set equal to  $0.0025 \text{ eV} \approx 29 k_B K$ . Resistivities calculated by Kubo-Greenwood formula are shown in Figure 5.11.



(a) Resistivities with normal scale, here the inset represents the same data but with a larger scale.

(b) Resistivities with logarithmic scale.

Figure 5.11: Resistivities of  $\text{EuTiO}_3$ . Solid lines represent theoretical results, and experimental data (dots) are plotted here for comparison.

It can be seen that this value of  $J$  fitted by experimental data is indeed small, this confirms our assumption. But, because the tiny subband is quite close to the Fermi level, such a small  $J$  still has a strong effect on the resistivity.

It is clear that such mechanism occurs in semiconductors and involves no strong intraatomic exchange interaction as in the double exchange model. Unlike in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  system which is metallic, the change in carrier density caused by the band shift plays a main role in the colossal magnetoresistance of  $\text{EuTiO}_3$ .

### The Value of Parameters

Here we shall discuss some details about the values of parameters  $\omega_0$  and  $g$ .

It has been mentioned earlier that the value of  $\omega_0$  is assumed to be the highest frequency optical phonon. The main reason is that the highest phonon band is well separated with other bands and is relatively flat. The flatness of the band indicates that the band is relatively local, which is consistent with the assumption of Holstein model.

The value of  $g$  is chosen to be 1 eV, it should be noted that this value is a large value for electron-phonon interaction. Especially, applying Lang-Firsov [118] transformation, which is the standard method for small polaron theory, on Holstein model yields some unphysical polaron parameters. The bandwidth renormalization constant for small polaron is  $\exp(-g^2/\omega_0^2) = \exp(-100) = 3.72 \times 10^{-44}$ , which means the bandwidth of polaron subband would be at the order of  $10^{-44}$  and thus this subband would be so fragile that it would be immediately washed out in a real material. However, Lang-Firsov transformation also shows the position of small polaron subband should be located around  $-g^2/\omega_0 = -10$  eV, which is far from the subband we obtain. Therefore what we obtain is not the fragile polaron subband but another relatively robust subband caused by strong electron-phonon interaction.

So is this large  $g$  possible? Our first principle calculation shows it is indeed possible in  $\text{EuTiO}_3$  system.

The DFT calculations are performed using Quantum ESPRESSO package [114]. The Troullier-Martins norm-conserving pseudopotentials with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals [115] are employed to describe the interactions between valence electrons in our system. The cutoff energies of plane waves are chosen as 80 Ry. A  $20 \times 20 \times 20$  Monkhorst-Pack  $k$ -point mesh is used for electronic self-consistent field calculations and a  $4 \times 4 \times 4$  Monkhorst-Pack  $k$ -point mesh is used for phonon calculations. The convergence threshold of energy is set to be  $10^{-14}$  Ry for electron, while for phonon calculations, the threshold is set to be  $10^{-18}$  Ry to get

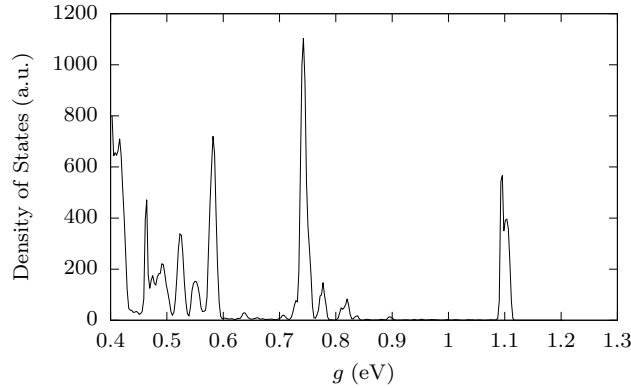


Figure 5.12: Density of states of the coupling constants between electronic states with localized LO mode phonon states. This calculation is done by Ji-Chang Ren.

a better convergence. The electron phonon coupling matrix is calculated by applying formula [119]:  $g_{m\nu}(\mathbf{k}, \mathbf{q}) = \langle u_{m\mathbf{k}+\mathbf{q}} | \Delta_{\mathbf{q}\nu} v^{\text{KS}} | u_{n\mathbf{k}} \rangle$ , where  $u_{n\mathbf{k}}$  is the lattice-periodic function in Bloch wavefunction, the bra and ket indicate an integral over one unit cell, and the operator  $\Delta_{\mathbf{q}\nu} v^{\text{KS}}$  is the derivative with a coefficient of the self-consistent potential with respect to a collective ionic displacement corresponding to a phonon with branch index  $\nu$  and momentum  $\mathbf{q}$ . In order to get a densier mesh to calculate the electron phonon coupling matrix, we apply Wannier interpolation technique, as implemented in EPW code [120]. After Fourier transformation back into momentum space, we obtain a dense  $40 \times 40 \times 40$   $\mathbf{k}$ -point mesh for states of electron and  $40 \times 40 \times 40$   $\mathbf{q}$ -point mesh for states of phonon.

The DFT results can be found in Fig. 5.12, it can be seen that the highest values of the elements of the electron-phonon coupling matrix elements are around 1.1 eV. Since Holstein model is used, in which electrons are coupled with localized phonons, we focus on the coupling between electrons and phonons of highest longitudinal optical mode. Therefore in Fig. 5.12 only those results of LO mode with coupling constant larger than 0.4 eV are represented. These results show that the value of  $g$  can reach about 1.1 eV, and thus our value is consistent with the DFT results.

### The Extreme Dilute Limit

In a strongly correlated system, usually the value of electron occupation number would greatly affect the electronic spectral density. For instance, the DMFT results for  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  system



[3–6] differ much around half filling situation for different occupation numbers.

However, in our calculations the rigid band approximation is applied, i.e., the spectral density remains unchanged when carrier density changes. Here we shall explain the reason why we can adopt this approximation.

It has been mentioned earlier that the electron occupation number per site at 20 K without the magnetic field is about  $8.457 \times 10^{-7}$ , and such small occupation number enables us to apply extreme dilute limit and single electron approximation used in DMFT for small polaron. In the presence of an external magnetic field, the occupation number increases dramatically. However, even the occupation increases 1000 times, it is at an order of  $10^{-4}$  which is still very small. Therefore we can say that during CMR the occupation number, although dramatically changes, is always small enough to apply extreme dilute limit and single electron approximation, and so the rigid band approximation. This is also an important difference between  $\text{EuTiO}_3$  system and  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ .

## 5.6 Results and Discussions

We have applied DFT+DMFT method to calculate the electronic structure of  $t_{2g}$  orbitals of Ti atom in  $\text{EuTiO}_3$ . Based on this electronic structure we have calculated the transport properties of  $\text{EuTiO}_3$  and explained the CMR in it. It is found that due to strong electron-phonon interaction the conduction band can form a tiny subband. This subband may be close to the Fermi level and responsible for conduction electrons. Since the subband is very small, the mobility of electrons in this subband would also be small. This is the reason why resistivities of  $\text{EuTiO}_3$  are quite high. Conduction electrons are also coupled with magnetic atoms via exchange interaction, and this interaction would slightly shift the electronic band when the material is magnetized. And because the subband is close to the Fermi level, a slight shift is enough to cause colossal magnetoresistance.

It is clear that this mechanism occurs in semiconductor and involves no strong intraatomic exchange interaction as in the double exchange model. Unlike in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  system which is metallic [3–7, 9–11], the change of carrier density caused by band shift plays a main role in the CMR of  $\text{EuTiO}_3$ . Besides, because at low temperature the carrier density for different electron spin changes dramatically when material is magnetized,  $\text{EuTiO}_3$  has a potential for spintronic device.

However, there are some flaws in our model. First, our model is a simplified model. It is not

enough to obtain really the fine electronic structure of  $\text{EuTiO}_3$ , thus the agreement with experimental data remains at a qualitative level. A more careful treatment on first principle calculation and DMFT procedure may improve the accuracy. Second, there are some arbitrariness in the choice of some parameters. There are four main parameters chosen by hand to fit the experiments:  $\mu$ ,  $J$ ,  $\omega_0$  and  $g$ . These arbitrariness weaken the reliability of our model. Experiments which can measure the carrier density change for different spin respectively, or just the total density change, in the presence of magnetic field can help to verify or falsify the validity of our theoretical description.

# Chapter 6

## Summary

In chapter 2–4 we have reviewed the theories needed for the final calculation for transport properties of  $\text{EuTiO}_3$ .

In chapter 2, a comprehensive review of transport theories is given. Among all these formulas, Einstein formula is adopted for simple fitting of experimental resistivities of  $\text{EuTiO}_3$ , and Kubo-Greenwood formula is used for final resistivity calculation.

In chapter 3, a brief introduction to dynamical mean-field theory based on Hubbard model is given. It gives the basic idea and a derivation of dynamical mean-field theory. In bulk system dynamical mean-field theory is, perhaps, the best method to handle strongly correlated electron systems until now. If we want to investigate the strong interaction in  $\text{EuTiO}_3$ , dynamical mean-field theory is needed. However, Hubbard model is not for a electron-phonon interaction system, and a dynamical mean-field theory for electron-phonon interaction is needed. In chapter 4 we briefly introduce dynamical mean-field theory for small polaron which is used for the Holstein model. Holstein model is the simplest model presents the electron-phonon interaction. This dynamical mean-field theory assumes single electron and zero temperature for electron. These two assumptions enable an impurity solver in real frequency domain, and this is the crucial advantage of the dynamical mean-field theory for small polaron.

In chapter 5, we introduce the magnetoresistance in  $\text{EuTiO}_3$ . At low temperature ( $< 40\text{ K}$ ), in the presence of external magnetic field the magnetization of  $\text{EuTiO}_3$  rises and the resistivity of  $\text{EuTiO}_3$  drops dramatically. The magnetization of  $\text{EuTiO}_3$  under different temperature and magnetic field is calculated by Weiss mean-field theory, the calculated results fit the experimental

data well. Based on the magnetization of  $\text{EuTiO}_3$  a simple fitting for the resistivity is done, which shows the change of carrier density due to the magnetization may be the essential reason of the colossal magnetoresistance. However, the simple fitting can not explain the very small mobility.

After taken strong electron-phonon interaction into consideration, we have applied DFT+DMFT method to calculate the electronic structure of  $t_{2g}$  orbitals of Ti atom in  $\text{EuTiO}_3$ . It is found that due to strong electron-phonon interaction the conduction band can form a tiny subband. Since the subband is very small, the mobility of electrons in this subband would be also small. This is the reason why resistivities of  $\text{EuTiO}_3$  are quite high. This subband may be close to the Fermi level. Conduction electrons are also coupled with magnetic atoms via exchange interaction, and this interaction would slightly shift the electronic band when the material is magnetized. And because the subband is close to the Fermi level, a slight shift is enough to cause dramatic carrier density change and thus colossal magnetoresistance. This mechanism occurs in semiconductor and involves no strong intraatomic exchange interaction as in the double exchange model. This is different from the mechanism of colossal magnetoresistance in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ .

Our model is a simplified model. It is not enough to obtain really the fine electronic structure of  $\text{EuTiO}_3$ , a more careful treatment on first principle calculation and dynamical mean-field theory procedure may improve the accuracy. Experiments which can measure the carrier density change for different spin respectively, or just the total density change, in the presence of magnetic field can help to verify or falsify the validity of our theoretical description. What's more, if our description is true, then because at low temperature the carrier density for different electron spin changes dramatically when the material is magnetized,  $\text{EuTiO}_3$  has a potential for spintronic device.

# Bibliography

- [1] L. M. Rodriguez-Martinez and J. P. Attfield, Phys. Rev. B **54**, R15622 (1996).
- [2] A. R. Ramirez, J. Phys. Condens. Matter, **9**, 8171 (1997).
- [3] A. J. Millis, P. B. Littlewood and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).
- [4] A. J. Millis, B. I. Shraiman and R. Mueller, Phys. Rev. Lett. **77**, 175 (1996).
- [5] A. J. Mills, R. Mueller and B. I. Shraiman, Phys. Rev. B. **54**, 5405 (1996).
- [6] A. J. Millis, Nature, **392**, 147 (1998).
- [7] J. Zang, A. R. Bishop and H. Röder, Phys. Rev. B. **53**, R8840 (1996).
- [8] H. Röder, J. Zang and A. R. Bishop, Phys. Rev. Lett, **76**, 1356 (1996).
- [9] Q. Li, J. Zang, A. R. Bishop, C. M. Soukoulis, Phys. Rev. B. **56**, 4541 (1997).
- [10] R. Shen and Z.-Z. Li, Solid State Commun. **110**, 237 (1999).
- [11] G.-M. Zhao, V. Smolyaninova, W. Prellier and H. Keller, Phys. Rev. Lett. **84**, 6086 (2000).
- [12] C. Zener, Phys. Rev. **82**, 403 (1951).
- [13] J. Kondo, Prog. Theor. Phys. **32**, 37 (1964).
- [14] K. Kubo and N. Ohata, J. Phys. Soc. Jpn., **33**, 21 (1972).
- [15] R. Chen, J. C. Ren, Km Rubi, R. Mahendiran and J.-S. Wang, arXiv:1703.02238 (2017).
- [16] Km Rubi and R. Mahendiran, arXiv:1612.09085 (2016).

- [17] R. Feynman, *The Feynman Lectures on Physics Volume I* (Addison Wesley Longman, 1970).
- [18] R. Brown, *Philos. Mag.* **4**, 161 (1828); **6**, 161 (1829).
- [19] A. Einstein, *Ann. Physik* **17**, 549 (1905); **19**, 371 (1906); *Investigations on the Theory of the Brownian Motion* (ed. by R. Fürth, Dover, New York, 1956).
- [20] M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.* **17**, 323 (1945).
- [21] L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics Volume 6: Fluid Mechanics* (Elsevier Pte Ltd., 1987).
- [22] R. Kubo, M. Toda and N. Hashitsume, *Statistical Physics II: Nonequilibrium Statistical Mechanics* (Springer-Verlag Berlin Heidelberg GmbH, 1991).
- [23] P. Drude, *Ann. Phys.* **306**, 566 (1900); *Ann. Phys.* **308**, 369 (1900)
- [24] E. M. Lifshitz and L. P. Pitaevskii, *Course of Theoretical Physics Volume 9: Statistical Physics part 2* (Elsevier, 1980).
- [25] L. D. Landau, *J. Exptl. Theoret. Phys. (U. S. S. R)* **30**, 1058 (1956); *J. Exptl. Theoret. Phys. (U. S. S. R)* **32**, 59 (1957); *J. Exptl. Theoret. Phys. (U. S. S. R)* **35**, 97 (1958); (English translations: *Soviet Phys. JETP* **3**, 920 (1957); **5**, 101 (1957); **8**, 70 (1958).)
- [26] E. Fermi, *Nuclear Physics* (University of Chicago Press, 1950).
- [27] P. Dirac, *Proc. R. Soc. A.* **114**, 243 (1927).
- [28] L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics Volume 3: Quantum Mechanics* (Elsevier, 1965).
- [29] L. Boltzmann, *Further Studies on the Thermal Equilibrium of Gas Molecules*, 1872.
- [30] G. D. Mahan, *Condensed Matter in a Nutshell* (Princeton University Press, 2011).
- [31] E. M. Lifshitz and L. P. Pitaevskii, *Course of Theoretical Physics Volume 10: Physical Kinetics* (Elsevier, 1981).

- [32] L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics Volume 5: Statistical Physics* (Elsevier, 1986).
- [33] W. Rhodes and M. Chase, *Rev. Mod. Phys.* **39**, 348 (1967).
- [34] H. A. Kramers, *Atti Cong. Intern. Fisici, Como.* **2**, 545 (1927).
- [35] R. de L. Kronig, *J. Opt. Soc. Am.* **12**, 547 (1926).
- [36] H. Nyquist, *Physical Review* **32**, 110 (1928).
- [37] H. B. Callen and T. A. Welton, *Physical Review* **83**, 34 (1951).
- [38] R. Kubo, *J. Phys. Soc. Jpn.* **12**, 570 (1957).
- [39] D. A. Greenwood, *Proc. Phys. Soc.* **71**, 585 (1958).
- [40] E. N. Economou *Green's Function in Quantum Physics* (Springer-Verlag, Berlin, 2006) 3rd ed.
- [41] D. J. Thouless, *Phil. Mag.* **32**, 877 (1975).
- [42] M. S. Green, *J. Chem. Phys.* **22**, 398 (1954).
- [43] P. B. Allen, Electron Transport, in *Conceptual Foundations of Material Properties: A standard model for calculation of ground- and excited-state properties*, M. L. Cohen and S. G. Louie, editors (Elsevier, Amsterdam, 2006), chapter 6.
- [44] H. Haug and A. P. Jauho, *Quantum Kinetics in Transport and Optics of Semiconductors* (Springer-Verlag Berlin, 2008)
- [45] S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, 1995).
- [46] J. Rammer, *Quantum Field Theory of Nonequilibrium States* (Cambridge University Press, 2007)
- [47] J.-S. Wang, B. K. Agarwalla, H. Li and J. Thingna, *Front. Phys.* **9**, 673 (2014).
- [48] L. P. Kadanoff, G. Baym and D. Pines, *Quantum Statistical Mechanics*, Westview Press, 1994.

- [49] L. Keldysh, Zh. Eksp. Teor. Fiz. **47**, 1515 (1964) [Engl. transl., Sov. Phys. JETP **20**, 1018 (1965)]
- [50] R. Mills, *Propagators for Quantum Statistical Physics* (unpublished, 1962).
- [51] J. M. Luttinger, **135**, A1505 (1964).
- [52] G. N. Lewis, M. Randall, K. S. Pitzer and L. Brewer, *Thermodynamics* (McGraw-Hill Book Co., New York, 1961).
- [53] P. Langevin, C. R. Acad. Sci. (Paris). **146**, 530 (1908); reviewed by D. S. Lemons and A. Gythiel, Am. J. Phys. **65**, 1079 (1997).
- [54] L. Onsager, Phys. Rev. **37**, 405 (1931).
- [55] A. Georges, G. Kotliar, W. Krauth and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
- [56] D. Vollhardt, Ann. Phys. **524**, 1 (2012).
- [57] P. W. Anderson, Phys. Rev. **124**, 41 (1961).
- [58] T. Matsubara, Prog. Theor. Phys. **14**, 351 (1955).
- [59] G. C. Wick, Phys. Rev. **96**, 1124 (1954).
- [60] J. Hubbard, Proc. R. Soc. A. **276**, 238 (1963).
- [61] R. P. Feynman and F. L. Vernon, Ann. Phys. **24**, 118 (1963).
- [62] R. M. Martin, *Electronic Structure: Basic Theory and Practical Methods* (Cambridge University Press, 2008).
- [63] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [64] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- [65] G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet and C. A. Marianetti, Rev. Mod. Phys. **78**, 865 (2006).
- [66] H. A. Bethe and H. H. Wills, Physica A. **391**, 3417 (1935).



- [67] M. Ostilli, *Physica A.* **391**, 3417 (2012).
- [68] J. Z. Zhao, J. N. Zhuang, X. Y. Deng, Y. Bi, L. C. Cai, Z. Fang and X. Dai, *Chin. Phys. B.* **21**, 057106 (2012).
- [69] J. K. Freericks, *Transport in Multilayered Nanostructures: The Dynamical Mean-Field Theory Approach* (Imperial College Press, 2016).
- [70] D. Bergeron and A.-M. S. Tremblay, *Phys. Rev. E* **94**, 023303 (2016).
- [71] R. P. Brent, *Algorithms for Minimization without Derivatives* (Prentice-Hall, New Jersey, 1973).
- [72] J. W. Negele and H. Orland, *Quantum Many-Particle Systems* (Westview Press, 1988).
- [73] G. C. Wick, *Phys. Rev.* **80**, 268 (1950).
- [74] A. Georges and G. Kotliar, *Phys. Rev. B* **45**, 6479 (1992).
- [75] R. J. Baxter, *Exactly Solved Models in Statistical Mechanics* (Academic Press, London, 1982)
- [76] J. Hubbard, *Proc. R. Soc. A.* **281**, 401 (1964).
- [77] A. N. Rubtsov, V. V. Savkin and A. I. Lichtenstein, *Phys. Rev. B* **72**, 035122 (2005)
- [78] P. Werner, A. Comanac, L. de Medici, M. Troyer and A. J. Millis, *Phys. Rev. Lett.* **92**, 076405 (2006).
- [79] E. Gull, A. J. Millis, A. I. Lichtenstein, A. N. Rubtsov, M. Troyer and P. Werner, *Rev. Mod. Phys.* **83**, 349 (2011).
- [80] J. E. Hirsch and R. M. Fye, *Phys. Rev. Lett.* **56**, 2521 (1986).
- [81] B. Bauer, L. D. Carr, A. Feiguin, J. Freire, S. Fuchs, L. Gamper, J. Gukelberger, E. Gull, S. Guertler *et al.* *J. Stat. Mech. Theor. Exp.* **2011**, P05001 (2011).
- [82] E. Gull, P. Werner, S. Fuchs, B. Surer, T. Pruschke, M. Troyer, *Comput. Phys. Commun.* **182**, 1078 (2011).

- [83] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka and J. Luitz, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Techn. Universitt Wien, Austria, 2011).
- [84] K. Haule, C.-H. Yee and K. Kim, *Phys. Rev. B* **81**, 195107 (2010).
- [85] O. Parcollet, M. Ferrero, T. Ayrat, H. Hafermann, I. Krivenko, L. Messio and P. Seth *et al.*, *Comput. Phys. Commun.* **196**, 398 (2015).
- [86] P. Seth, I. Krivenko, M. Ferrero, O. Parcollet *et al.*, *Comput. Phys. Commun.* **200**, 274 (2016).
- [87] M. Aichhorn, L. Pourovskii, P. Seth, V. Vildosla *et al.*, *Comput. Phys. Commun.* **204**, 200 (2016).
- [88] X. Gonze, B. Amadon, P. M. Anglade, J.-M. Beuken, F. Bottin, P. Boulanger, F. Bruneval *et al.*, *Comput. Phys. Commun.* **180**, 2582 (2009).
- [89] L. Huang, Y.-L. Wang, Z.-Y. Meng, L. Du, P. Werner and X. Dai, *Comput. Phys. Commun.* **195**, 140 (2015).
- [90] L. D. Landau, *Phys. Z. Sowjetunion.* **3**, 644 (1933).
- [91] L. D. Landau and S. I. Pekar, *Zh. Eksp. Teor. Fiz.* **18**, 419 (1948); English translation: *Ukr. J. Phys.*, Special Issue, **53**, 71 (2008).
- [92] S. Ciuchi, F. de Pasquale and S. Fratini and D. Feinberg, *Phys. Rev. B* **56**, 4494 (1997).
- [93] S. Fratini and S. Ciuchi, *Phys. Rev. Lett.* **91**, 256403 (2003).
- [94] T. Holstein, *Ann. Phys.* **8**, 325 (1959).
- [95] T. Holstein, *Ann. Phys.* **8**, 343 (1959).
- [96] V. S. Viswanath and G. Müller, *The Recursion Method* (Springer-Verlag, Berlin, 1994).
- [97] W. Thomson, *Proc. Royal Soc. London*, **8**, 546 (1856).
- [98] M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich and J. Chazelas, *Phys. Rev. Lett.* **61**, 2472 (1988)

- [99] G. Binasch, P. Grünberg, F. Saurenbach and W. Zinn, Phys. Rev. B **39**, 4828R (1989).
- [100] G. H. Jonker and J. H. Van Santen, Physica, **16**, 337 (1950).
- [101] S. Jin, H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, L. H. Chen, Nature, **264**, 413 (1994).
- [102] B. P. Alho, A. M. G. Carvalho, P. J. von Ranke, J. Magn. Magn. Mater. **324**, 210 (2012).
- [103] P. J. von Ranke, B. P. Alho, E. P. Nóbrega, V. S. R. de Sousa, T. S. T. Alvarenga, A. M. G. Carvalho, N. A. de Oliveira, J. Magn. Magn. Mater. **324**, 1290 (2012).
- [104] P. J. von Ranke, S. Gama, P. O. Ribeiro, A. M. G. Carvalho, B. P. Alho, T. S. T. Alvarenga, E. P. Nobrega, A. Caldas, V. S. R. de Sousa, P. H. O. Lopes and N. A. de Oliveira, J. Appl. Phys. **118**, 243901 (2015).
- [105] A. Midya, P. Mandal, Kim Rubi, R. Chen, J.-S. Wang, R. Mahendiran, C. Lorusso and M. Evangelisti, Phys. Rev. B, **93**, 094422 (2016).
- [106] T. Katsufuji and H. Takagi, Phys. Rev. B **64**, 054415 (2001).
- [107] C. Haas, CRC. Crit. Rev. Solid State. Sci. **1**, 47 (1970).
- [108] R. Ranjan2009, H. S. Nabi and R. Pentcheva, J. Appl. Phys. **105**, 053905 (2009).
- [109] J. H. Lee, L. Fang, E. Vlahos, X. Ke, Y. W. Jung, L. F. Kourkoutis, J. W. Kim, P. J. Ryan, M. Roeckerath, V. Goian, M. Bernhagen *et. al*, Nature, **466**, 954 (2010).
- [110] V. N. Bogomolov and D. N. Mirlin, Phys. Stat. Sol. **27**, 443 (1968).
- [111] V. N. Bogomolov, Yu. A. Firsov, E. K. Kudinov and D. N. Mirlin, Phys. Stat. Sol. **35**, 555 (1969).
- [112] G. D. Mahan, *Many-Particle Physics* (Plenum Press, New York, 2000), 3rd ed.
- [113] K. Z. Rushchanskii, N. A. Spaldin and M. Ležaić, Phys. Rev. B. **85**, 104109 (2012).
- [114] P. Giannozzi *et al.*, J. Phys. Condens. Matter **21**, 395502 (2009).
- [115] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996)

- [116] N. Marzari and D. Vanderbilt, *Phys. Rev. B* **56**, 12847 (1997).
- [117] I. Souza, N. Marzari and D. Vanderbilt, *Phys. Rev. B* **65**, 035109 (2001).
- [118] I. G. Lang and Yu. A. Firsov, *Zh. Eksp. Teor. Fiz.* **43**, 1843 (1962) [*Sov. Phys. JETP* **16**, 1301 (1963)].
- [119] F. Giustino, *Rev. Mod. Phys.* **89**, 015003 (2017).
- [120] S. Ponc e, E. R. Margine, C. Verdi and F. Giustino, *Comput. Phys. Commun.* **209**, 116 (2016).