Chapter 2

Theory

2.1 Electron Tunneling Spectroscopy

In classical mechanics, a particle whose total energy is below the energy potential of a barrier can not penetrate through it. But in quantum mechanics, the particle has finite probability to pass through the barrier [22].

Consider two metal leads separated by a thin insulator which serves as a potential barrier as shown in Fig. 2.1 (a). Its band diagram is shown in Fig. 2.1 (b). In Fig. 2.1 (b), a electron wave incident from the left, defined as e^{ikx}, suffers partial reflection with amplitude R at $x = 0$, is exponential decaying, $e^{-\kappa x}$, in the interval $0 < x < t$, and emerges for $x > t$ as Te^{iqx}. D, the transmission factor, is defined as the ratio of the incident probability current $\hbar k/m_1$ to the transmission probability current $T^2\hbar q/m_2$. In the case of small transmission, the exact expression for D is [23, 24]:

$$D(E_x) = ge^{-2K}, \tag{2.1}$$

where

$$g = \frac{16kq\kappa^2}{(k^2+\kappa^2)(q^2+\kappa^2)}, \tag{2.2}$$

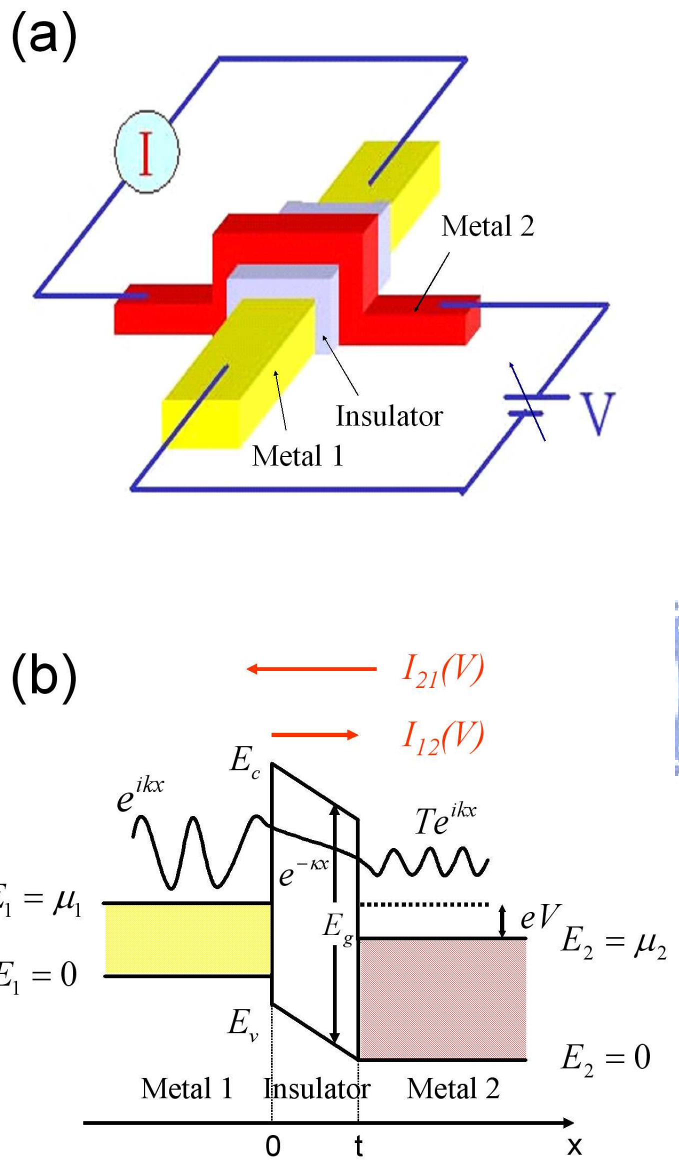

Figure 2.1: (a) A M-I-M tunnel junction. (b) The band diagram of the M-I-M tunnel junction.

$$
\begin{aligned}
K &= \int_0^t \kappa(x, E_x)dx, &(2.3)\\
\kappa(x, E_x) &= (\frac{2m}{\hbar^2})^{1/2}[U(x) - E_x]^{1/2}, &(2.4)\\
E_x &= \frac{\hbar^2 k_x^2}{2m}. &(2.5)
\end{aligned}
$$

where m is the effective mass of the tunneling electron, $U(x)$ is the potential energy of the barrier, and E_x and k_x are the energy and wavevector of the tunneling electron in the tunneling direction (the $\hat{x}$ direction) respectively.

The magnitude of the transmission factor is dependent on the thickness and height of the barrier. The thicker the barrier thickness or the higher the potential energy, the smaller the magnitude.

2.1.1 Tunneling between Two Free-Electron Metals

The General Expression for the Tunneling Current

The electrons in either one lead can tunnel through the barrier to the other one. The net current is obtained by subtracting one from the other. Without any bias, the magnitudes of these two opposite current are equal, and the net current is zero since in this case the Fermi energy of these two lead are equal ($\mu_1 = \mu_2$). But if a nonzero bias voltage is applied between these two leads, the Fermi energy of them are not equal. In this case the magnitudes of these two opposite current are not equal and will cause a net current.

As shown in Fig. 2.1 (b), if a positive bias is applied to lead 2 (i.e. treating lead 1 as ground), it will lower the Fermi level of lead 2 by eV. Here we use the convention $e > 0$, i.e., $e = 1.6 \times 10^{-19}$ Coul.. Therefore we have

$$\mu_2 = \mu_1 - eV. \tag{2.6}$$

The Fermi-Dirac distribution function in these two leads are

$$f_1 = \frac{1}{1+e^{\frac{E-\mu_1}{k_B T}}} \equiv f(E), \tag{2.7}$$

$$f_2 = \frac{1}{1+e^{\frac{E-\mu_2}{k_B T}}} = \frac{1}{1+e^{\frac{E-\mu_1+eV}{k_B T}}} \equiv f(E+eV), \tag{2.8}$$

and the transmission factor D is a function of E_x and V under nonzero bias, expressed as $D(E_x, V)$.

The electrical current density tunneling from lead 1 to lead 2, $J_{1\to 2}$, can be expressed as [23]

$$J_{1\to 2}(V) = \frac{-2e}{(2\pi)^3}\int_{k_x}\int_{k_y}\int_{k_z} dk_x dk_y dk_z v_x D(E_x, V) f(E)[1 - f(E+eV)]. \tag{2.9}$$

Since

$$\frac{dk_y dk_z}{(2\pi)^2} = \rho_t dE_t, \tag{2.10}$$

and

$$v_x = \frac{1}{\hbar}\frac{\partial E}{\partial k_x}, \tag{2.11}$$

where ρ_t and E_t is the two dimensional density of states and the energy corresponding to wavevector k_t respectively in the transverse direction which is perpendicular to $\hat{x}$, substituting these in (2.9), we obtain

$$J_{1\to 2}(V) = \frac{-2e\rho_t}{h}\int_{E_x}\int_{E_t} dE_x dE_t D(E_x, V) f(E)[1 - f(E+eV)]. \tag{2.12}$$

Similarly, the electrical current density tunneling from lead 2 to lead 1 can be expressed as

$$J_{2\to 1}(V) = \frac{-2e\rho_t}{h}\int_{E_x}\int_{E_t} dE_x dE_t D(E_x, V) f(E+eV)[1 - f(E)]. \tag{2.13}$$

The net current density from lead 2 to lead 1, $J(V)$, can be obtained as

$$\begin{aligned} J(V) &\equiv J_{2\to 1}(V) - J_{1\to 2}(V) \\ &= \frac{2e\rho_t}{h}\int_{E_x}\int_{E_t} dE_x dE_t D(E_x,V)[f(E) - f(E+eV)]. \end{aligned} \tag{2.14}$$

Note that for positive bias applied to lead 2, the net current from lead 2 to lead 1 is positive which can be seen from (2.14), and this is in agreement with our common sense.

At low temperature limit, $T \to 0$, all electrons lie below Fermi energy, and only the electrons whose total energy E $(= E_x + E_t)$ is between $\mu - eV$ (here we let $\mu_1 = \mu$) and μ can participate in tunneling. In this case, (2.14) can be reduced to

$$J(V) = \frac{2e\rho_t}{h}\int_{E_x}\int_{E_t} dE_x dE_t D(E_x,V), \tag{2.15}$$

and the integral is taken within the range $\mu - eV \leq E = E_x + E_t \leq \mu$. As shown in Fig. 2.2, the region of integral can be divided into two parts, region 1 and 2. Therefore (2.15) can be written as

$$\begin{aligned} J(V) &= \frac{2e\rho_t}{h}[\int_0^{\mu-eV} D(E_x,V)dE_x \int_{\mu-eV-E_x}^{\mu-E_x} dE_t \quad \text{Region I} \\ &\quad + \int_{\mu-eV}^{\mu} D(E_x,V)dE_x \int_0^{\mu-E_x} dE_t] \quad \text{Region II.} \end{aligned} \tag{2.16}$$

After performing the transverse integral, (2.16) reduces to

$$J(V) = \frac{2e\rho_t}{h}[eV\int_0^{\mu-eV} D(E_x,V)dE_x + \int_{\mu-eV}^{\mu} D(E_x,V)(\mu - E_x)dE_x]. \tag{2.17}$$

Note that the derivation of (2.17) is based on the assumption $T \to 0$, and the expression is valid whether the barrier is symmetric or not. Actually, the barrier information has been included in $D(E_x,V)$.

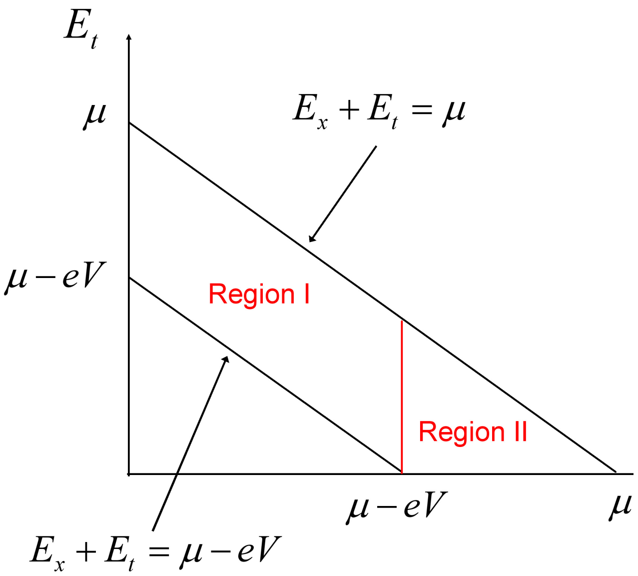

Figure 2.2: The integration range of Eq. (2.15).

Simmon's Simplification

Simmons [25] calculated (2.17) further. He defined the barrier height $\phi(x)$ as

$$\phi(x) = U(x) - \mu. \tag{2.18}$$

For simplification, he roughly estimated the average value $\bar{\phi}$ of the barrier height

$$\bar{\phi} = \frac{1}{t}\int_0^t \phi(x)dx. \tag{2.19}$$

From (2.3), (2.4), (2.18), and (2.19),

$$\begin{aligned} K &= \int_0^t \frac{(2m)^{\frac{1}{2}}}{\hbar}[U(x) - E_x]^{\frac{1}{2}}dx \\ &= \frac{(2m)^{\frac{1}{2}}}{\hbar}\int_0^t [\phi(x) + \mu - E_x]^{\frac{1}{2}}dx \\ &\approx \frac{(2m)^{\frac{1}{2}}\beta t}{\hbar}(\bar{\phi} + \mu - E_x)^{\frac{1}{2}}, \end{aligned} \tag{2.20}$$

where β is a correction factor which is usually near unity.

Under the application of positive V to lead 2, the average value of the barrier height is

$$\begin{aligned}\bar{\phi}(V) &= \frac{1}{t}\int_0^t \phi(x) - \frac{eVx}{t}dx \\ &= \frac{1}{t}\int_0^t \phi(x)dx - \frac{eV}{t^2}\int_0^t xdx \\ &= \bar{\phi} - \frac{eV}{2}, \end{aligned} \tag{2.21}$$

and K in (2.20) can be written as

$$\begin{aligned}K(V) &\approx \frac{(2m)^{\frac{1}{2}}\beta t}{\hbar}[\bar{\phi}(V) + \mu - E_x]^{\frac{1}{2}} \\ &= \frac{(2m)^{\frac{1}{2}}\beta t}{\hbar}(\bar{\phi} - \frac{eV}{2} + \mu - E_x)^{\frac{1}{2}}, \end{aligned} \tag{2.22}$$

if $\bar{\phi}$ in (2.20) is replaced with $\bar{\phi}(V)$ in (2.21). Using the approximation $g \approx 1$ and substituting (2.22) in (2.1), he obtained

$$D(E_x) \approx \exp[-(\frac{4\pi\beta t}{h})(2m)^{\frac{1}{2}}(\bar{\phi} - \frac{eV}{2} + \mu - E_x)^{\frac{1}{2}}]. \tag{2.23}$$

Substituting (2.23) in (2.17), the tunneling current density as a function of bias voltage $J(V)$ is obtained as

$$\begin{aligned}J(V) &= \frac{e}{2\pi h(\beta t)^2}\{(\bar{\phi} - \frac{eV}{2})\exp[-\frac{4\pi\beta t}{h}(2m)^{\frac{1}{2}}(\bar{\phi} - \frac{eV}{2})^{\frac{1}{2}}] \\ &\quad -(\bar{\phi} + \frac{eV}{2})\exp[-\frac{4\pi\beta t}{h}(2m)^{\frac{1}{2}}(\bar{\phi} + \frac{eV}{2})^{\frac{1}{2}}]\}, \end{aligned} \tag{2.24}$$

which, for low voltages, reduces to

$$J(V) = \alpha V + \gamma V^3 + \cdots, \tag{2.25}$$

where α and γ are given by

$$\alpha = \frac{(2m)^{\frac{1}{2}}}{t}(\frac{e}{h})^2\bar{\phi}^{\frac{1}{2}}\exp(-A\bar{\phi}^{\frac{1}{2}}), \tag{2.26}$$

$$\frac{\gamma}{\alpha} = \frac{(Ae)^2}{96\bar{\phi}} - \frac{Ae^2}{32\bar{\phi}^{\frac{1}{2}}}. \tag{2.27}$$

Therefore, the differential conductance can be obtained as

$$G(V) \equiv \frac{\partial J}{\partial V} = \alpha + 3\gamma V^2 + \cdots, \tag{2.28}$$

which is a parabolic function of V and is symmetric to zero-bias.

Note that the parabolic behavior in (2.28) is due to the low voltages approximation and its symmetry to zero-bias is due to the average barrier height $\bar{\phi}(V)$ simplification in (2.22) therefore in transmission factor (2.23).

BDR Model

Let us consider a metal-insulator-metal tunnel junction with an asymmetric barrier as shown in Fig. 2.3. Without application of bias and in thermal equilibrium, the Fermi levels in metal 1 and in metal 2 are equal as shown in Fig. 2.3. The barrier height seen from these two leads are different due to their unequal work functions, and are ϕ_1 from lead 1 and ϕ_2 from lead 2 respectively. According to Simmons' derivation, the tunneling current $J(V)$ is asymmetric to V and therefore the differential conductance $G(V)$ is symmetric to V whether the barrier is symmetric or not, which can be seen in (2.25) and (2.28) respectively. But in our common sense, the magnitudes of $J(V)$ and $J(-V)$ should not be equal (i.e. $J(V) \neq -J(-V)$) due to the asymmetric barrier. For an asymmetric barrier, $J(V)$ is not asymmetric and therefore $G(V)$ is not symmetric. The contradiction comes from Simmons' $\bar{\phi}(V)$ simplification in (2.21) $\sim$ (2.24).

Brinkman, Dynes, and Rowell [26] used a simple model of an asymmetric barrier (BDR model) as shown in Fig. 2.3. The barrier height measured from the Fermi level in lead 1 under the application of bias V to lead 2 is

$$\phi(x,V) = \phi_1 + \frac{x}{t}(\phi_2 - eV - \phi_1). \tag{2.29}$$

After substituting (2.29) in (2.1) to get $D(E_x, V)$ and then substituting the calculated $D(E_x, V)$ in (2.17), they obtained $J(V)$. Differential conductance $G(V)$ was obtained through calculating $\partial J/\partial V$, and they got, for low voltages,

$$G(V) = G(0)[1 - (\frac{A_0 \Delta\phi}{16\bar{\phi}^{3/2}})eV + (\frac{9{A_0}^2}{128\bar{\phi}})(eV)^2], \tag{2.30}$$

where

$$\bar{\phi} = \frac{\phi_1 + \phi_2}{2}, \tag{2.31}$$
$$\Delta\phi = \phi_2 - \phi_1, \tag{2.32}$$
$$A_0 = \frac{4(2m)^{1/2}t}{3\hbar}, \tag{2.33}$$

and $G(0)$ is the conductance at zero-bias.

Note that in low temperature limit and for low voltages, $G(V)$ calculated by BDR model which considered an asymmetric barrier is approximately a parabolic function of V and its minimum does not occur at zero-bias. For a symmetric barrier, $\Delta\phi = \phi_1 - \phi_2 = 0$, $G(V)$ is symmetric to zero-bias which is obvious in (2.30) and this is in agreement with our common sense.

Thermal Effect

The derivations above (both Simmons' simplification and BDR model) are under the $T \to 0$ approximation. What is the temperature dependence of the tunneling

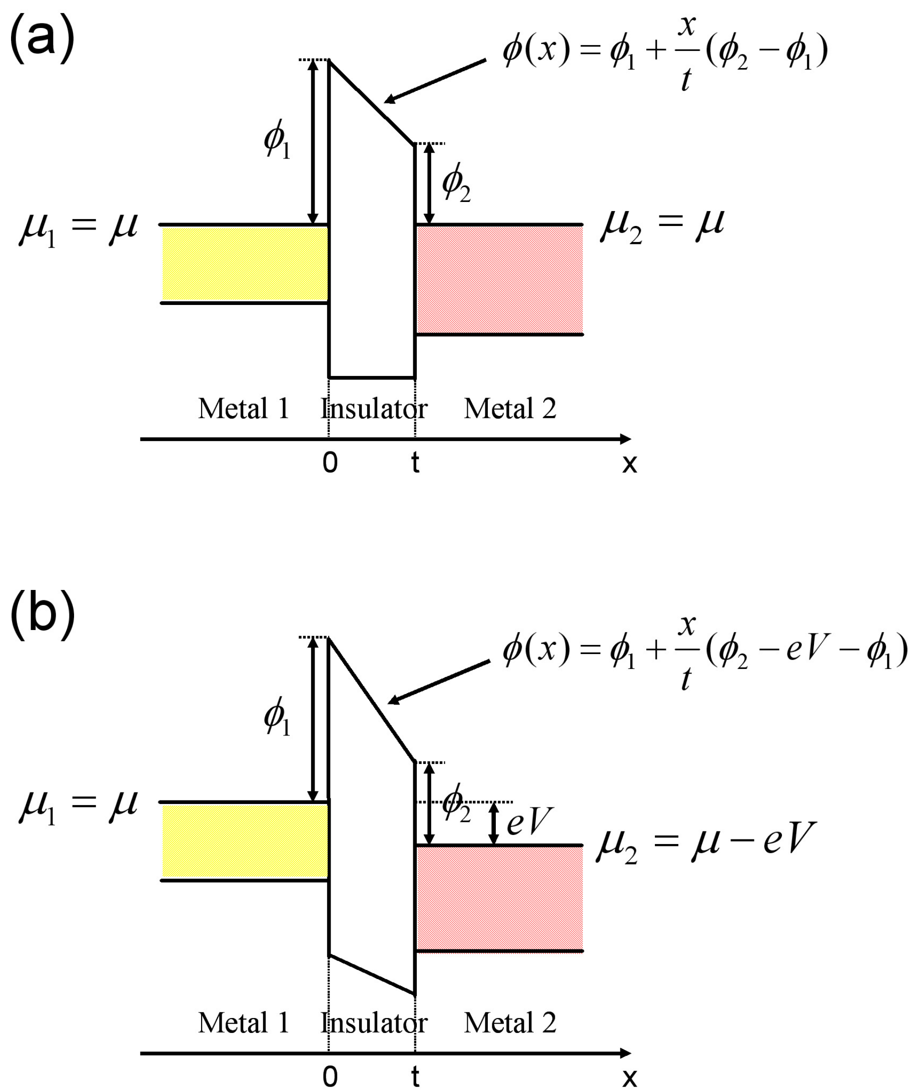

Figure 2.3: The asymmetric barrier.

(a) $V = 0$, the Fermi levels in these two leads are equal, $\mu_1 = \mu_2 = \mu$. The barrier height seen from lead 1 is just a function of x, $\phi(x) = \phi_1 + x/t(\phi_2 - \phi_1)$ (b) With a positive bias applied to lead 2, the Fermi level in lead 2 is lowered by eV, and the barrier height seen from lead 1 is not only a function of x but also of V, $\phi(x, V) = \phi_1 + x/t(\phi_2 - eV + \phi_1)$.

current? Simmons [27] included the temperature effect in his calculation which was based on $\bar{\phi}(V)$ simplification, and obtained

$$
\begin{aligned}
J(V,T) &= J(V,0)\frac{\pi c_1 kT}{\sin(\pi c_1 kT)} && (2.34)\\
&\approx J(V,0)[1+\frac{1}{6}(\pi c_1 kT)^2+\cdots], && (2.35)
\end{aligned}
$$

where

$$
c_1 \approx \frac{\beta t}{\hbar}(\frac{2m}{\bar{\phi}})^{1/2}. \qquad (2.36)
$$

Therefore,

$$
\begin{aligned}
G(V,T) &\equiv \frac{\partial J(V,T)}{\partial V} \\
&= \frac{\partial J(V,0)}{\partial V}\frac{\pi c_1 kT}{\sin(\pi c_1 kT)} \\
&= G(V,0)\frac{\pi c_1 kT}{\sin(\pi c_1 kT)} && (2.37)\\
&\approx G(V,0)[1+\frac{1}{6}(\pi c_1 kT)^2+\cdots]. && (2.38)
\end{aligned}
$$

Although Simmons' simplification can not explain the offset of the parabolic dependence of $G(V)$, the temperature dependence (2.39) is correct, in an asymmetric barrier case. Therefore, combined with BDR model (2.30) (in (2.30), $G(0)$ now becomes $G(0,0)$), we have

$$
\begin{aligned}
G(V,T) &= G(V,0)\frac{\pi c_1 kT}{\sin(\pi c_1 kT)} \\
&= \{G(0,0)[1-(\frac{A_0\Delta\phi}{16\bar{\phi}^{3/2}})eV+(\frac{9{A_0}^2}{128\bar{\phi}})(eV)^2]\}\frac{\pi c_1 kT}{\sin(\pi c_1 kT)} \\
&= G(0,T)[1-(\frac{A_0\Delta\phi}{16\bar{\phi}^{3/2}})eV+(\frac{9{A_0}^2}{128\bar{\phi}})(eV)^2], && (2.39)
\end{aligned}
$$

where

$$
G(0,T) = G(0,0)\frac{\pi c_1 kT}{\sin(\pi c_1 kT)}. \qquad (2.40)
$$

Note that the result (2.39) is based on the assumption that the two leads separated by the potential barrier are free-electron metals. In addition, (2.39) can be employed to determine the height and width of a barrier. Fitting the $G(V,T)$ curve at some fixed T by (2.39), A_0, $\bar{\phi}$, and $\Delta\phi$, and therefore the width , ϕ_1, and ϕ_2 (through (2.31) $\sim$ (2.33)), can be obtained.

2.1.2 Density of States Effect and Assisted Tunneling

In section 2.1.1, we considered the tunneling current in a tunnel junction with two free-electron metal leads. The transmission factor depended on just the height and thickness of the barrier and on the energy of the incident electron. The calculation was carried out using a stationary-state method. If these two leads are not free-electron metals (the density of states effect should be considered) or some additional interaction exerting on the tunneling electrons (not only the influence of barrier but also the contribution of the interaction should be considered), how these affect the tunneling current?

Transfer Hamiltonian Calculations

Let us consider the tunneling effect in another viewpoint as shown in Fig. 2.4 (a). The leads are two nearly independent portions separated by the barrier, and the weak coupling between them can be treated by a perturbing Hamiltonian H^C. If electrons tunnel through a barrier with an additional interaction exerted on them, H^C can be viewed as the superposition of two parts, the contribution due to the barrier, H^B, and due the additional interaction, H^{Int}. The total Hamiltonian can

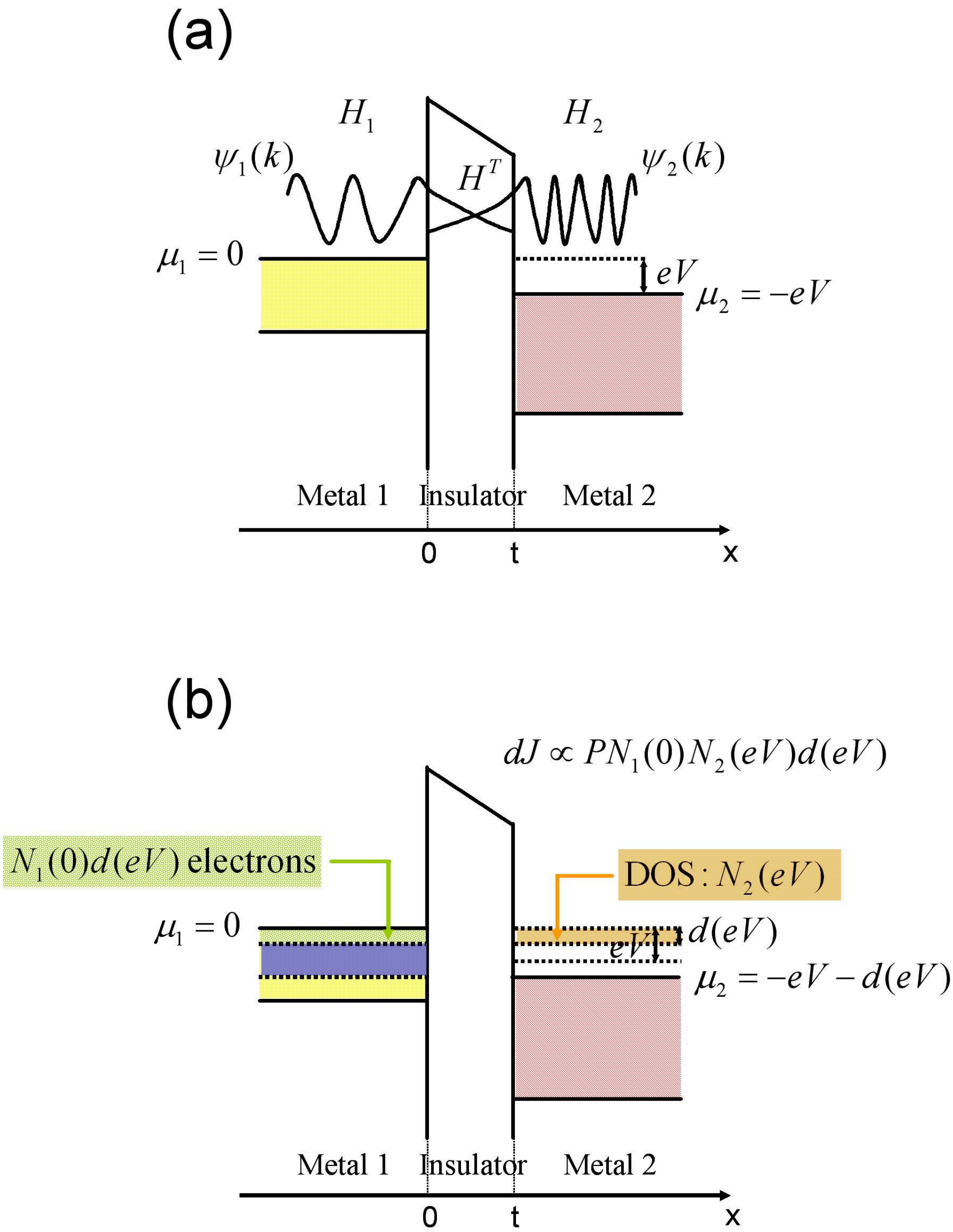

Figure 2.4: (a) Transfer-Hamiltonian model. (b) $G(V)$ as $T \to 0$.

be expressed as

$$
\begin{aligned}
H &= H_1 + H_2 + H^C &(2.41)\\
&= H_1 + H_2 + (H^B + H^{Int}), &(2.42)
\end{aligned}
$$

where H_1 and H_2 are the Hamiltonians of the electrons in lead 1 and lead 2 respectively, and $H^C = H^B + H^{Int}$. Then the transition rate $W^C_{k_1k_2}$ from a given state $|k_1\rangle$ in lead 1 with energy ϵ_1 to a state $|k_2\rangle$ with energy ϵ_2 in lead 2 is

$$
\begin{aligned}
W^C_{k_1k_2} &= \frac{2\pi}{\hbar}|\langle k_2|H^C|k_1\rangle + \cdots|^2\delta(\epsilon_{k_1} - \epsilon_{k_2})\\
&= \frac{2\pi}{\hbar}|\langle k_2|(H^B + H^{Int})|k_1\rangle + \cdots|^2\delta(\epsilon_{k_1} - \epsilon_{k_2})\\
&= \frac{2\pi}{\hbar}|\langle k_2|H^B|k_1\rangle + \langle k_2|H^{Int}|k_1\rangle + \cdots|^2\delta(\epsilon_{k_1} - \epsilon_{k_2})\\
&= \frac{2\pi}{\hbar}(|\langle k_2|H^B|k_1\rangle|^2 + |\langle k_2|H^{Int}|k_1\rangle|^2 + ***)\delta(\epsilon_{k_1} - \epsilon_{k_2})\\
&= W^{B,1st}_{k_1k_2} + W^{Int,1st}_{k_1k_2} + ***, &(2.43)
\end{aligned}
$$

where

$$
\begin{aligned}
W^{B,1st}_{k_1k_2} &= \frac{2\pi}{\hbar}|\langle k_2|H^B|k_1\rangle|^2\delta(\epsilon_{k_1} - \epsilon_{k_2}) = P^{B,1st}_{k_1k_2}\delta(\epsilon_{k_1} - \epsilon_{k_2}), &(2.44)\\
W^{Int,1st}_{k_1k_2} &= \frac{2\pi}{\hbar}|\langle k_2|H'|k_1\rangle|^2\delta(\epsilon_{k_1} - \epsilon_{k_2}) = P^{Int,1st}_{k_1k_2}\delta(\epsilon_{k_1} - \epsilon_{k_2}), &(2.45)
\end{aligned}
$$

are the transition rates in first order from state $|k_1\rangle$ in lead 1 to state $|k_2\rangle$ in lead 2 due to the barrier and the additional interaction respectively, $P^{B,1st}_{k_1k_2}$ and $P^{Int,1st}_{k_1k_2}$ are the corresponding matrix elements' squares which are proportional to the transition rates, "$\cdots$" represents the second and higher order coefficients in Born's approximation and therefore "$***$" includes the interference between them.

Under the application of a positive bias V to lead 2, the electrical current density tunneling from lead 1 to lead 2, $J_{1\to 2}$, can be expressed as [23]

$$\begin{aligned} J_{1\to 2}(V) &= -2e\sum_{k_1,k_2} W^{C}_{k_1k_2} f(\epsilon_{k_1})[1-f(\epsilon_{k_2}+eV)] && (2.46)\\ &\approx -2e\sum_{k_1,k_2} (W^{B,1st}_{k_1k_2}+W^{Int,1st}_{k_1k_2}) f(\epsilon_{k_1})[1-f(\epsilon_{k_2}+eV)] \\ &= J^{B}_{1\to 2}(V)+J^{Int}_{1\to 2}(V) && (2.47) \end{aligned}$$

where the pre-factor 2 is due to the spin degeneracy, and

$$\begin{aligned} J^{B}_{1\to 2}(V) &= -2e\sum_{k_1,k_2} W^{B,1st}_{k_1k_2} f(\epsilon_{k_1})[1-f(\epsilon_{k_2}+eV)], && (2.48)\\ J^{Int}_{1\to 2}(V) &= -2e\sum_{k_1,k_2} W^{Int,1st}_{k_1k_2} f(\epsilon_{k_1})[1-f(\epsilon_{k_2}+eV)]. && (2.49) \end{aligned}$$

Here e is the positive electron charge ($e = 1.6\times 10^{-19}$ Coul.), f is the Fermi-Dirac distribution, V is the applied voltage. Similarly, the electrical current tunneling from lead 1 to lead 2, $J_{2\to 1}$, can be expressed as

$$J_{2\to 1}(V) = J^{B}_{2\to 1}(V)+J^{Int}_{2\to 1}(V) \tag{2.50}$$

where

$$\begin{aligned} J^{B}_{2\to 1}(V) &= -2e\sum_{k_1,k_2} W^{B,1st}_{k_2k_1} f(\epsilon_{k_2}+eV)[1-f(\epsilon_{k_1})], && (2.51)\\ J^{Int}_{2\to 1}(V) &= -2e\sum_{k_1,k_2} W^{Int,1st}_{k_2k_1} f(\epsilon_{k_2}+eV)[1-f(\epsilon_{k_1})]. && (2.52) \end{aligned}$$

Subtracting $J_{1\to 2}$ from $J_{2\to 1}$, we get the net electrical current

$$\begin{aligned} J(V) &= J_{2\to 1}(V)-J_{1\to 2}(V)\\ &= [J^{B}_{2\to 1}(V)-J^{B}_{1\to 2}(V)]+[J^{Int}_{2\to 1}(V)-J^{Int}_{1\to 2}(V)] \end{aligned}$$

$$
\begin{aligned}
&= 2e\sum_{k_1,k_2} W_{k_1k_2}^{B,1st}[f(\epsilon_{k_1}) - f(\epsilon_{k_2}+eV)] \\
&\quad +2e\sum_{k_1,k_2} W_{k_1k_2}^{Int,1st}[f(\epsilon_{k_1}) - f(\epsilon_{k_2}+eV)] \\
&= J^B(V) + J^{Int}(V), \qquad (2.53)
\end{aligned}
$$

where

$$
\begin{aligned}
J^B(V) &= 2e\sum_{k_1,k_2} W_{k_1k_2}^{B,1st}[f(\epsilon_{k_1}) - f(\epsilon_{k_2}+eV)], \qquad (2.54) \\
J^{Int}(V) &= 2e\sum_{k_1,k_2} W_{k_1k_2}^{Int,1st}[f(\epsilon_{k_1}) - f(\epsilon_{k_2}+eV)], \qquad (2.55)
\end{aligned}
$$

are the tunneling current due to the barrier and due to the additional interaction respectively. In the above derivation, we used the relations $W_{k_1k_2}^{B,1st} = W_{k_2k_1}^{B,1st}$ and $W_{k_1k_2}^{Int,1st} = W_{k_2k_1}^{Int,1st}$, which are obvious from (2.44) and (2.45) respectively. Using (2.44), (2.54) can be expressed as

$$
\begin{aligned}
J^B(V) &= 2e\int\int W_{k_1k_2}^{B,1st}[f(\epsilon_{k_1}) - f(\epsilon_{k_2}+eV)]N_1(\epsilon_{k_1})N_2(\epsilon_{k_2}+eV)d\epsilon_{k_1}d\epsilon_{k_2} \\
&= 2e\int\int P_{k_1k_2}^{B,1st}\delta(\epsilon_{k_1}-\epsilon_{k_2})[f(\epsilon_{k_1}) - f(\epsilon_{k_2}+eV)] \\
&\qquad\qquad N_1(\epsilon_{k_1})N_2(\epsilon_{k_2}+eV)d\epsilon_{k_1}d\epsilon_{k_2} \\
&= 2e\int P_{k_1k_2}^{B,1st}[f(\epsilon_{k_1}) - f(\epsilon_{k_1}+eV)]N_1(\epsilon_{k_1})N_2(\epsilon_{k_1}+eV)d\epsilon_{k_1} \\
&= 2e\int P_{k_1k_2}^{B,1st}[f(\epsilon) - f(\epsilon+eV)]N_1(\epsilon)N_2(\epsilon+eV)d\epsilon. \qquad (2.56)
\end{aligned}
$$

Similarly, using (2.45), (2.55) can be expressed as

$$
J^{Int}(V) = 2e\int P_{k_1k_2}^{Int,1st}[f(\epsilon) - f(\epsilon+eV)]N_1(\epsilon)N_2(\epsilon+eV)d\epsilon. \qquad (2.57)
$$

For generality, we assume lead 1 and lead 2 may not be free-electron metals, and the DOS in them can be expressed as the summation of the DOS for a free-electron metal (N^0) and the corresponding correction (ΔN), i.e. $N_1(\epsilon) = N_1^0(\epsilon) + \Delta N_1(\epsilon)$ and $N_2(\epsilon) = N_2^0(\epsilon) + \Delta N_2(\epsilon)$ respectively. Here N_1^0 and N_2^0 are the corresponding DOS for the free-electron metal case, and therefore have little dependence on energy. Then, the net tunneling current density can be expressed as:

$$
\begin{aligned}
J(V) &= J^B(V) + J^{Int}(B) \\
&= 2e\int P_{k_1k_2}^{B,1st}[f(\epsilon) - f(\epsilon+eV)][N_1^0(\epsilon) + \Delta N_1(\epsilon)] \\
&\qquad\qquad \times [N_2^0(\epsilon+eV) + \Delta N_2(\epsilon+eV)]d\epsilon \\
&= 2e\int P_{k_1k_2}^{B,1st}[f(\epsilon) - f(\epsilon+eV)]N_1^0(\epsilon)N_2^0(\epsilon+eV)d\epsilon \\
&\quad +2e\int P_{k_1k_2}^{B,1st}[f(\epsilon) - f(\epsilon+eV)]N_1^0(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon \\
&\quad +2e\int P_{k_1k_2}^{B,1st}[f(\epsilon) - f(\epsilon+eV)]\Delta N_1(\epsilon)N_2^0(\epsilon+eV)d\epsilon \\
&\quad +2e\int P_{k_1k_2}^{B,1st}[f(\epsilon) - f(\epsilon+eV)]\Delta N_1(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon \\
&\quad +2e\int P_{k_1k_2}^{Int,1st}[f(\epsilon) - f(\epsilon+eV)]N_1^0(\epsilon)N_2^0(\epsilon+eV)d\epsilon \\
&\quad +2e\int P_{k_1k_2}^{Int,1st}[f(\epsilon) - f(\epsilon+eV)]N_1^0(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon \\
&\quad +2e\int P_{k_1k_2}^{Int,1st}[f(\epsilon) - f(\epsilon+eV)]\Delta N_1(\epsilon)N_2^0(\epsilon+eV)d\epsilon \\
&\quad +2e\int P_{k_1k_2}^{Int,1st}[f(\epsilon) - f(\epsilon+eV)]\Delta N_1(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon.
\end{aligned}
\tag{2.58}
$$

As $T \to 0$, (2.58) can be reduced to

$$
\begin{aligned}
J(V) &= 2e\int_{-eV}^{0} P^{B,1st}N_1^0(\epsilon)N_2^0(\epsilon+eV)d\epsilon \\
&\quad +2e\int_{-eV}^{0} P^{B,1st}N_1^0(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon
\end{aligned}
$$

$$
\begin{aligned}
&+2e\int_{-eV}^{0} P^{B,1st}\Delta N_1(\epsilon)N_2^0(\epsilon+eV)d\epsilon \\
&+2e\int_{-eV}^{0} P^{B,1st}\Delta N_1(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon \\
&+2e\int_{-eV}^{0} P^{Int,1st}N_1^0(\epsilon)N_2^0(\epsilon+eV)d\epsilon \\
&+2e\int_{-eV}^{0} P^{Int,1st}N_1^0(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon \\
&+2e\int_{-eV}^{0} P^{Int,1st}\Delta N_1(\epsilon)N_2^0(\epsilon+eV)d\epsilon \\
&+2e\int_{-eV}^{0} P^{Int,1st}\Delta N_1(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon \\
= \; & J^B_{free}(V)+J^B_{\Delta N_2}(V)+J^B_{\Delta N_1}(V)+J^B_{\Delta N_1,\Delta N_2}(V) \\
&+J^{Int}_{free}(V)+J^{Int}_{\Delta N_2}(V)+J^{Int}_{\Delta N_1}(V)+J^{Int}_{\Delta N_1,\Delta N_2}(V), \qquad (2.59)
\end{aligned}
$$

where we use the approximation $P^{B,1st}_{k_1k_2} = P^{B,1st}$ and $P^{Int,1st}_{k_1k_2} = P^{Int,1st}$. Here

$$
\begin{aligned}
J^B_{free}(V) &= 2e\int_{-eV}^{0} P^{B,1st}N_1^0(\epsilon)N_2^0(\epsilon+eV)d\epsilon, \qquad (2.60) \\
J^B_{\Delta N_2}(V) &= 2e\int_{-eV}^{0} P^{B,1st}N_1^0(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon \\
&= 2e\int_{0}^{eV} P^{B,1st}N_1^0(0)\Delta N_2(\epsilon')d\epsilon', \qquad (2.61) \\
J^B_{\Delta N_1}(V) &= 2e\int_{-eV}^{0} P^{B,1st}\Delta N_1(\epsilon)N_2^0(\epsilon+eV)d\epsilon \\
&= 2e\int_{-eV}^{0} P^{B,1st}\Delta N_1(\epsilon)N_2^0(0)d\epsilon, \qquad (2.62) \\
J^B_{\Delta N_1,\Delta N_2}(V) &= 2e\int_{-eV}^{0} P^{B,1st}\Delta N_1(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon, \qquad (2.63) \\
J^{Int}_{free}(V) &= 2e\int_{-eV}^{0} P^{Int,1st}(\epsilon+eV)N_1^0(\epsilon)N_2^0(\epsilon+eV)d\epsilon \\
&= 2e\int_{0}^{eV} P^{Int,1st}(\epsilon')N_1^0(0)N_2^0(0)d\epsilon', \qquad (2.64)
\end{aligned}
$$

$$
\begin{aligned}
J^{Int}_{\Delta N_2}(V) &= 2e\int_{-eV}^{0} P^{Int,1st}(\epsilon+eV)N_1^0(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon \\
&= 2e\int_{0}^{eV} P^{Int,1st}(\epsilon')N_1^0(0)\Delta N_2(\epsilon')d\epsilon', &(2.65)\\
J^{Int}_{\Delta N_1}(V) &= 2e\int_{-eV}^{0} P^{Int,1st}\Delta N_1(\epsilon)N_2^0(\epsilon+eV)d\epsilon, &(2.66)\\
J^{Int}_{\Delta N_1,\Delta N_2}(V) &= 2e\int_{-eV}^{0} P^{Int,1st}\Delta N_1(\epsilon)\Delta N_2(\epsilon+eV)d\epsilon, &(2.67)
\end{aligned}
$$

where we use the approximations $N_1^0(\epsilon) = N_1^0(0)$ since the DOS for a free-electron metal has little dependence on energy, and the the Fermi energy is set to be 0. We note $J^B_{free}(V)$, as expressed in (2.60), can be reduced to (2.17) [24] and therefore the corresponding differential conductance $G^B_{free}(V)$ is parabolic for low voltages.

Now, we will consider the following two cases.

Case 1:

There is no additional interaction exerted on the tunneling electrons ($H^{Int} = 0$ and therefore $P^{Int,1st} = 0$). In this case, $J^{Int}_{free}(V) = J^{Int}_{\Delta N_2}(V) = J^{Int}_{\Delta N_1}(V) = J^{Int}_{\Delta N_1,\Delta N_2}(V) = 0$, and therefore the net tunneling current density

$$
\begin{aligned}
J(V) &= J^B_{free}(V) + J^B_{\Delta N_2}(V) + J^B_{\Delta N_1}(V) + J^B_{\Delta N_1,\Delta N_2}(V) \\
&\approx J^B_{free}(V) + J^B_{\Delta N_2}(V) + J^B_{\Delta N_1}(V) \\
&= J^B_{free}(V) + 2e\int_0^{eV} P^{B,1st}N_1^0(0)\Delta N_2(\epsilon')d\epsilon' \\
&\quad +2e\int_{-eV}^{0} P^{B,1st}\Delta N_1(\epsilon)N_2^0(0)d\epsilon. &(2.68)
\end{aligned}
$$

Here we neglect the term $J^B_{\Delta N_1,\Delta N_2}(V)$ since it contains second order correction as shown in (2.63). The differential conductance

$$
G(V) \equiv \frac{\partial J}{\partial V}
$$

$$
\begin{aligned}
&\approx G^{B}_{free}(V) + G^{B}_{\Delta N_2}(V) + G^{B}_{\Delta N_1}(V) \\
&= G^{B}_{free}(V) + 2e^2 P^{B,1st} N^0_1(0)\Delta N_2(eV) \\
&\quad +2e^2 P^{B,1st}\Delta N_1(-eV) N^0_2(0). \qquad (2.69)
\end{aligned}
$$

It means that in this case, through the $G(V)$ measurements, the obtained spectra contain the magnitudes of the correction of the DOS in lead 1 and lesd 2 respectively superposed on a parabolic background, $G^{B}_{free}(V)$, as shown in (2.69).

Case 2:

Lead 1 and lead 2 are free-electron metals, and there is an additional interaction exerted on the tunneling electrons. In this case, $\Delta N_1 = \Delta N_2 = 0$, and therefore $J^{B}_{\Delta N_2}(V) = J^{B}_{\Delta N_1}(V) = J^{B}_{\Delta N_1,\Delta N_2}(V) = J^{Int}_{\Delta N_2}(V) = J^{Int}_{\Delta N_1}(V) = J^{Int}_{\Delta N_1,\Delta N_2}(V) = 0$, which are obvious from (2.61), (2.62), (2.63), (2.65), (2.66), and (2.67), respectively. Then, the net tunneling current

$$
\begin{aligned}
J(V) &= J^{B}_{free}(V) + J^{Int}_{free}(V) \\
&= J^{B}_{free}(V) + 2e\int_0^{eV} P^{Int,1st}(\epsilon')N^0_1(0)N^0_2(0)d\epsilon'. \qquad (2.70)
\end{aligned}
$$

The differential conductance

$$
\begin{aligned}
G(V) &\equiv \frac{\partial J}{\partial V} \\
&= G^{B}_{free}(V) + G^{Int}_{free}(V) \\
&= G^{B}_{free}(V) + 2e^2 P^{Int,1st}(eV)N^0_1(0)N^0_2(0). \qquad (2.71)
\end{aligned}
$$

It means that in this case, through the $G(V)$ measurements, the obtained spectrum contains $G^{Int}_{free}(V)$, which is proportional to the transition rate due to the additional interaction exerted on the tunneling electrons, superposed on a parabolic background, $G^{B}_{free}(V)$.

2.2 Kondo Effect in Bulk Samples

2.2.1 Weak Coupling Regime

In 1964, J. Kondo [7] considered the problem that how free electrons interact with the dilute localized magnetic impurities. He write the total Hamiltonian as the summation of the free electron energy, H_0, and the interaction between the free electrons and the localized magnetic impurities, H'. The interaction between these impurities can be neglected since the their concentration is dilute. The total Hamiltonian H can be expressed as

$$H = H_0 + H', \tag{2.72}$$

where

$$\begin{aligned} H_0 &= \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma}, \\ H' &= J \sum_{\mathbf{k}\mathbf{k}'} [(a^\dagger_{\mathbf{k}'\uparrow} a_{\mathbf{k}\uparrow} - a^\dagger_{\mathbf{k}'\downarrow} a_{\mathbf{k}\downarrow}) S_z + (a^\dagger_{\mathbf{k}'\uparrow} a_{\mathbf{k}\downarrow}) S_- + (a^\dagger_{\mathbf{k}'\downarrow} a_{\mathbf{k}\uparrow}) S_+]. \end{aligned} \tag{2.73}$$

Here $J > 0$ for antiferromagnetic coupling. He treated H' as a perturbative term and calculated the scattering rate (transition rate) from an initial state i to a final state n, $W_{i\to n}$, to second order Born's approximation:

$$W_{i\to n} \approx \frac{2\pi}{\hbar} |H'_{ni} + \sum_m \frac{H'_{nm} H'_{mi}}{E_i - E_m}|^2 \delta(E_n - E_i) \tag{2.74}$$

$$\approx \frac{2\pi}{\hbar} [H'_{ni} H'_{in} + (\sum_m \frac{H'_{nm} H'_{mi} H'_{in}}{E_i - E_m} + \text{c.c.})] \delta(E_n - E_i), \tag{2.75}$$

where the first and second terms in the "$|\cdots|$" of (2.74) are the first and second order Born's approximation respectively. The second term in the square brackets of (2.75) is the interference between the first and second order Born's approximation.

After substituting (2.73) in to (2.75), the scattering rate can be calculated, and therefore the resistance can be obtained as

$$R_{sd}(T) = R_{1st}(1 - 2J\rho \log \frac{k_B T}{D}), \tag{2.76}$$

where ρ is the density of states around Fermi surface in the host metal. D is the conduction band width in the host metal. R_{1st} is the resistance contributed from the 1st order Born's approximation, while $R_{1st} 2J\rho \log(k_B T/D)$ is the resistance contributed from the interference between the 1st and 2nd Born's approximation. Note that R_{1st} is constant to T, and $R_{sd}(T)$ has $-\log T$ dependence.

2.2.2 Strong Coupling Regime

As mentioned above, for noninteracting localized spins in bulk samples, the additional resistance R_{sd} due the $s - d$ exchange interaction can be calculated perturbatively to second order Born's approximation, and can be expressed as (2.76). If we inspect the second term "$-2J\rho \log \frac{k_B T}{D}$" in the parentheses of (2.76), we will find it is positive because $J > 0$ and $\log(k_B T/D) < 0$ ($\because k_B T < D$), and its magnitude increases as T decreases. Eventually the second term will be comparable to the first term at some sufficient low temperature, namely Kondo temperature, T_K. T_K is defined as

$$-2J\rho \log \frac{k_B T_K}{D} = 1. \tag{2.77}$$

Solve (2.77) and we will obtain

$$T_K = \frac{D}{k_B} e^{-\frac{1}{2J\rho}}. \tag{2.78}$$

Below T_K, the second term in the parentheses of (2.76) will be larger than the first term, and the perturbation method starts to lose its validity. Moreover, the second term will diverge and cause an infinite resistance as $T \to 0$. The unphysical result is due to only the leading order in the perturbation calculation was included in (2.76), and can be avoided by a complete summation of *all* the orders in the perturbation [28, 29, 30, 31]. Considering all the parquet diagrams, Hamann [29] obtained an approximate expression for the resistivity:

$$R_{Hamann}(T) = \frac{R_0}{2}\{1 - \frac{\ln(T/T_K)}{[(\ln(T/T_K))^2 + \pi^2 S(S+1)]^{1/2}}\}. \quad (2.79)$$

For $T \ll T_K$, (2.79) can be expanded to give

$$R_{Hamann}(T)|_{T \ll T_K} = R_0\{1 - \frac{\pi^2 S(S+1)}{4(\ln(T/T_K))^2} + \frac{3(\pi^2 S(S+1))^2}{16(\ln(T/T_K))^4} + \cdots\}, \quad (2.80)$$

which is an even function to T, and can be fitted to a simple power law,

$$\begin{aligned} R_{Hamann}(T)|_{T \ll T_K} &= R_0\{1 - (\frac{T}{\theta_R})^2 + O(\frac{T}{\theta_R})^4 + \cdots\} \\ &\approx R_0[1 - (\frac{T}{\theta_R})^2] \\ &= a - bT^2. \end{aligned} \quad (2.81)$$

Therefore, in the low temperature limit, the resistance has T^2 dependence, and this can be explained by the Fermi liquid theory [32].

As $T = 0$, the system reaches to its ground state. What is the nature of the ground state? Yosida [9], using variational methods and considering the $S = 1/2$ model, demonstrated that the ground state is singlet for the antiferromagnetic coupling.

Although Hamann considered all the parquet diagrams, and obtained (2.79) which can approximately describe the resistance from weak to strong coupling regime, the more precise results can be acquired by the numerical renormalization group (NRG) methods [32, 13, 33]. An empirical expression for the NRG calculation is [21]:

$$R_{NRG,empirical}(T) = R_0(\frac{T_0^2}{T^2 + T_0^2})^{\alpha}, \tag{2.82}$$

where T_0 relates to T_K through

$$T_0 = T_K/\sqrt{2^{1/\alpha} - 1}, \tag{2.83}$$

and $\alpha \approx 0.2 \pm 0.01$ for the $S = 1/2$ case.

The expressions (2.79) for $S = 1/2$ and (2.82) are plotted together in Fig. 2.5. We can see that for $0.5 \lesssim T/T_K \lesssim 5$, these two expressions are very close, but (2.79) fails at low temperatures. We should note that at low temperatures, these two expressions both have "$-T^2$" dependence as shown in Fig. 2.5.

2.3 Kondo Effect in Tunnel Junctions

2.3.1 Weak Coupling Regime

In 1967 Appelbaum [2] considered the problem what is the influence on the tunneling current if some magnetic impurities localized inside the barrier as shown in Fig. 2.6. The Hamiltonian can be written as

$$H = \sum_i \frac{p_i^2}{2m} + \sum_i V(\mathbf{x_i}) + \frac{1}{2}\sum_{i \neq j} W(\mathbf{x_i} - \mathbf{x_j}), \tag{2.84}$$

in second-quantized form it becomes

$$H = H_0 + H_I, \tag{2.85}$$

$$H_0 = \int \psi^{\dagger}(\mathbf{x})(\frac{p^2}{2m} + \sum_i V(\mathbf{x}))\psi(\mathbf{x})d^3x, \tag{2.86}$$

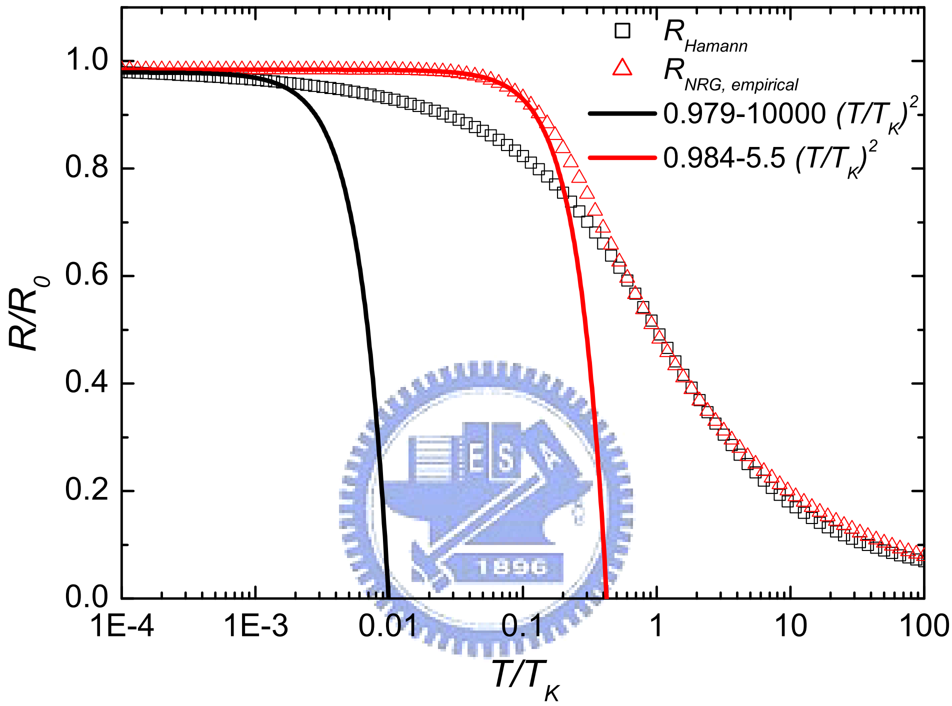

Figure 2.5: The plots of of $R_{Hamann}(T/T_K)$ and $R_{NRG}(T/T_K)$.
For $0.5 \lesssim T/T_K \lesssim 5$, these two expressions are very close, but R_{Hamann} fails at low temperatures. We should note that at low temperatures, these two expressions both have "$-T^2$" dependence.

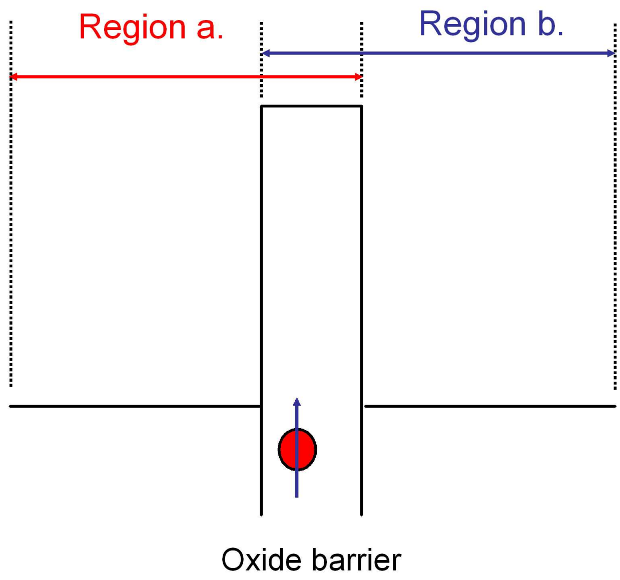

Figure 2.6: A schematic representation of a tunnel junction which contains a magnetic impurity in its barrier.

$$H_I = \frac{1}{2} \int \psi^\dagger(\mathbf{x})\psi^\dagger(\mathbf{x}')W(\mathbf{x}-\mathbf{x}')\psi(\mathbf{x}')\psi(\mathbf{x})d^3x, \tag{2.87}$$

where

$$\psi(\mathbf{x}) = \sum_i a_i\psi_i^a(\mathbf{x}) + \sum_i b_i\psi_i^b(\mathbf{x}), \tag{2.88}$$

$$\psi^\dagger(\mathbf{x}) = \sum_i a_i^\dagger\psi_i^{a\dagger}(\mathbf{x}) + \sum_i b_i^\dagger\psi_i^{b\dagger}(\mathbf{x}). \tag{2.89}$$

The $\psi_i^a(\mathbf{x})$ are a complete set of states in the region a of Fig. **??** and the $\psi_i^b(\mathbf{x})$ are a complete set of states in the region b. Therefore,

$$\psi(\mathbf{x}) = \sum_{\mathbf{k},\sigma} a_{\mathbf{k}\sigma}\psi_{\mathbf{k}\sigma}^a(\mathbf{x}) + \sum_{\mathbf{k}',\sigma'} b_{\mathbf{k}'\sigma'}\psi_{\mathbf{k}'\sigma'}^b(\mathbf{x}) + \sum_{\sigma} d_\sigma\psi_{d\sigma}(\mathbf{x}) \tag{2.90}$$

where $\{\psi_{\mathbf{k}\sigma}^a(\mathbf{x})\}$ and $\{\psi_{\mathbf{k}\sigma}^a(\mathbf{x})\}$ are the conduction electron states on side a and b respectively, and $\{\psi_{d\sigma}(\mathbf{x})\}$ are the localized electron states. Here only one localized state is assumed for simplicity. $a_{\mathbf{k}\sigma}$ and $b_{k\sigma}$ are destruction operators for an electron with momentum $\mathbf{k}$ and spin σ on side a and b respectively, and d_σ is the destruction operator for an electron in a localized state. Substitute $\psi(\mathbf{x})$ and $\psi^\dagger(\mathbf{x})$ into (2.85) $\sim$ (2.87), the following form can be obtained:

$$H = H_1 + H_2 + H_3 + H_4 + \cdots, \tag{2.91}$$

where

$$H_1 = \sum_{\mathbf{k},\sigma} \epsilon^a_{\mathbf{k}\sigma} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} + \sum_{\mathbf{k},\sigma} \epsilon^b_{\mathbf{k}\sigma} b^\dagger_{\mathbf{k}\sigma} b_{\mathbf{k}\sigma}, \tag{2.92}$$

This is the single-particle conduction-electron energies.

$$\begin{aligned} H_2 \;\; = \;\; & \sum_{\mathbf{k},\mathbf{k}',\sigma} (T_{\mathbf{k}\mathbf{k}'} a^\dagger_{\mathbf{k}\sigma} b_{\mathbf{k}'\sigma} + T_{\mathbf{k}'\mathbf{k}} b^\dagger_{\mathbf{k}'\sigma} a_{\mathbf{k}\sigma}) & (2.93) \\ & + \sum_{\mathbf{k},\sigma} T^a_{\mathbf{k},d} (a^\dagger_{\mathbf{k}\sigma} d_\sigma + d^\dagger_\sigma a_{\mathbf{k}\sigma}) & (2.94) \\ & + \sum_{\mathbf{k},\sigma} T^b_{\mathbf{k},d} (b^\dagger_{\mathbf{k}\sigma} d_\sigma + d^\dagger_\sigma b_{\mathbf{k}\sigma}), & (2.95) \end{aligned}$$

H_2 arises from single-particle terms in the Hamiltonian. (2.93) is due to the direct overlap of the conduction electron states on sides a and b as they tail into the barrier. (2.94) and (2.95) are due to the overlap of the localized d states with the conduction electrons on the a and b sides respectively.

$$H_3 = \sum_{\sigma} E_d n_\sigma + U n_\sigma n_{-\sigma}, \tag{2.96}$$

where U is the direct Coulomb integral between the localized electrons, E_d is the appropriate single particle energies for the localized electrons and $n_\sigma = d^\dagger_\sigma d_\sigma$.

$$H_5 = \sum_{\mathbf{k},\mathbf{k}',\sigma,\sigma'} W_{d,\mathbf{k};d,\mathbf{k}'} d^\dagger_\sigma a^\dagger_{\mathbf{k}\sigma'} d_{\sigma'} a_{\mathbf{k}'\sigma} \quad (2.97)$$

$$+ \sum V^a_{\mathbf{k},d}(d^\dagger_\sigma a_{\mathbf{k}\sigma} + a^\dagger_{\mathbf{k}\sigma} d_\sigma). \quad (2.98)$$

Since the localized electron is near to side a, the coupling between electrons on side b and the localized electron is very small. A term which is first order in this coupling, the product of three electron operators for side b and one localized electron operator is retained. Therefore he obtained

$$H_6 = \sum_{\mathbf{k},\sigma} V^b_{\mathbf{k},d}(d^\dagger_\sigma b_{\mathbf{k}\sigma} + b^\dagger_{\mathbf{k}\sigma} d_\sigma). \quad (2.99)$$

H_7 includes terms in which conduction-electron operators for sides a and b along with localized electrons operators appears. Among these he retained only

$$H_7 = \sum_{\mathbf{k},\mathbf{k}',\sigma,\sigma'} W_{\mathbf{k},d;\mathbf{k}',d} a^\dagger_{\mathbf{k}\sigma} d^\dagger_{\sigma'} b_{\mathbf{k}'\sigma'} d_\sigma + \textit{Hermitian conjugate} \quad (2.100)$$

$$+ \sum_{\mathbf{k},\mathbf{k}',\sigma,\sigma'} W_{\mathbf{k},d;d,\mathbf{k}'} a^\dagger_{\mathbf{k}\sigma} d^\dagger_{\sigma'} d_{\sigma'} b_{\mathbf{k}'\sigma} + \textit{Hermitian conjugate}. \quad (2.101)$$

He replaced the d operator by spin operator in (2.97) and (2.100), obtaining

$$J_a \sum_{\mathbf{k},\mathbf{k}'} \{S_z(a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}'\uparrow} - a^\dagger_{\mathbf{k}\downarrow} a_{\mathbf{k}'\downarrow}) + S^+ a^\dagger_{\mathbf{k}\downarrow} a_{\mathbf{k}'\uparrow} + S^- a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}'\downarrow}\}$$
$$+T_{Ja} \sum_{\mathbf{k},\mathbf{k}'} \{S_z[(a^\dagger_{\mathbf{k}\uparrow} b_{\mathbf{k}'\uparrow} + b^\dagger_{\mathbf{k}'\uparrow} a_{\mathbf{k}\uparrow}) - (a^\dagger_{\mathbf{k}\downarrow} b_{\mathbf{k}'\downarrow} + b^\dagger_{\mathbf{k}'\downarrow} a_{\mathbf{k}\downarrow})]$$
$$+S^+(a^\dagger_{\mathbf{k}\downarrow} b_{\mathbf{k}'\uparrow} + b^\dagger_{\mathbf{k}'\downarrow} a_{\mathbf{k}\uparrow}) + S^-(a^\dagger_{\mathbf{k}\uparrow} b_{\mathbf{k}'\downarrow} + b^\dagger_{\mathbf{k}'\uparrow} a_{\mathbf{k}\downarrow})\}, \quad (2.102)$$

in addition he had

$$T \sum_{\mathbf{k},\mathbf{k}',\sigma} (a^\dagger_{\mathbf{k}\sigma} b_{\mathbf{k}'\sigma} + b^\dagger_{\mathbf{k}'\sigma} a_{\mathbf{k}\sigma}) + T_a \sum_{\mathbf{k},\mathbf{k}',\sigma} (a^\dagger_{\mathbf{k}\sigma} b_{\mathbf{k}'\sigma} + b^\dagger_{\mathbf{k}'\sigma} a_{\mathbf{k}\sigma}). \quad (2.103)$$

The first term of (2.103) is just (2.93), and the second term represents all the nonexchange mechanisms for the tunneling of an electron from side a to side bin which the conduction electron interacts with the localized electron. Equations (2.91), (2.102) and (2.103) together make up the complete model Hamiltonian.

In a magnetic field $\mathbf{H}$, and with a bias voltage V applied to side a, the Hamiltonian of the system can be written as

$$
\begin{aligned}
H &= H_0 + H', && (2.104)\\
H_0 &= \sum_{\mathbf{k},\sigma} \tilde{\epsilon}^a_{\mathbf{k}\sigma} a^\dagger_{\mathbf{k}\sigma} a_{\mathbf{k}\sigma} + \sum_{\mathbf{k},\sigma} \epsilon^b_{\mathbf{k},\sigma} b^\dagger_{\mathbf{k}\sigma} b_{\mathbf{k}\sigma} + g|\mu_B|\mathbf{S}\cdot\mathbf{H}, && (2.105)\\
H' &= H^T + H^I, && (2.106)\\
H^T &= T_{Ja} \sum_{\mathbf{k},\mathbf{k}'} \{ S_z[(a^\dagger_{\mathbf{k}\uparrow} b_{\mathbf{k}'\uparrow} + b^\dagger_{\mathbf{k}'\uparrow} a_{\mathbf{k}\uparrow}) - (a^\dagger_{\mathbf{k}\downarrow} b_{\mathbf{k}'\downarrow} + b^\dagger_{\mathbf{k}'\downarrow} a_{\mathbf{k}\downarrow})] && (2.107)\\
&\quad + S^+(a^\dagger_{\mathbf{k}\downarrow} b_{\mathbf{k}'\uparrow} + b^\dagger_{\mathbf{k}'\downarrow} a_{\mathbf{k}\uparrow}) + S^-(a^\dagger_{\mathbf{k}\uparrow} b_{\mathbf{k}'\downarrow} + b^\dagger_{\mathbf{k}'\uparrow} a_{\mathbf{k}\downarrow}) \} && (2.108)\\
&\quad + T \sum_{\mathbf{k},\mathbf{k}',\sigma} (a^\dagger_{\mathbf{k}\sigma} b_{\mathbf{k}'\sigma} + b^\dagger_{\mathbf{k}'\sigma} a_{\mathbf{k}\sigma}) + T_a \sum_{\mathbf{k},\mathbf{k}',\sigma} (a^\dagger_{\mathbf{k}\sigma} b_{\mathbf{k}'\sigma} + b^\dagger_{\mathbf{k}'\sigma} a_{\mathbf{k}\sigma}), && (2.109)\\
H^I &= J_a \sum_{\mathbf{k},\mathbf{k}'} \{ S_z(a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}'\uparrow} - a^\dagger_{\mathbf{k}\downarrow} a_{\mathbf{k}'\downarrow}) + S^+ a^\dagger_{\mathbf{k}\downarrow} a_{\mathbf{k}'\uparrow} + S^- a^\dagger_{\mathbf{k}\uparrow} a_{\mathbf{k}'\downarrow} \}, && (2.110)
\end{aligned}
$$

where $\epsilon^a_{\mathbf{k}\sigma}$ and $\epsilon^b_{\mathbf{k}\sigma}$ implicitly include the Zeemann energy and

$$\tilde{\epsilon}^a_{\mathbf{k}\sigma} = \epsilon^a_{\mathbf{k}\sigma} + eV. \qquad (2.111)$$

Assume $\mathbf{H} = H\hat{z}$, the last term in (2.105) takes the form

$$g|\mu_B|\mathbf{S}\cdot\mathbf{H} = \Delta S_z, \qquad (2.112)$$

where the Zeemann splitting energy $\Delta \equiv g\mu_B H$.

The total current J_{ab} between sides a and b can be calculated by multiplying the current j_{ab} which is due to a single magnetic impurity by N_a, the number of localized spin on side a. j_{ab} can be calculated from

$$j_{ab} = e\sum_{M} P_M \sum_{\mathbf{k},\mathbf{k}',\sigma,\sigma'} [W_{\mathbf{k}\sigma M;\mathbf{k}'\sigma' M'} f(\epsilon^a_{\mathbf{k}\sigma})(1-f(\epsilon^b_{\mathbf{k}'\sigma'}))] \tag{2.113}$$

$$-e\sum_{M'} P_{M'} \sum_{\mathbf{k},\mathbf{k}',\sigma,\sigma'} [W_{\mathbf{k}'\sigma' M';\mathbf{k}\sigma M} f(\epsilon^b_{\mathbf{k}'\sigma'})(1-f(\epsilon^a_{\mathbf{k}\sigma}))], \tag{2.114}$$

where e is the charge of the electron ($e = -1.6\times 10^{-19}$ coul.), P_M is the statistical probability for $S_z = M$, and $f(\epsilon_{\mathbf{k}})$ is the Fermi-Dirac distribution function. $W_{\mathbf{k}\sigma M;\mathbf{k}'\sigma' M'}$ is the transition probability per unit time that a conduction electron in state $(\mathbf{k},\sigma)$ on side a scatters into state $(\mathbf{k}',\sigma')$ on side b, with the localized spin undergoing the transition $M \to M'$. Since spin is conserved

$$\sigma + M = \sigma' + M' \tag{2.115}$$

$W_{\mathbf{k}'\sigma' M';\mathbf{k}\sigma M}$ has a similar meaning for transition from side b to side a.

In the weak coupling regime, similar to the method used by Kondo [7], Appelbaum [2] calculated the transition rate W to second order Born's approximation, and obtained the tunneling current. The tunneling current contains three parts, the contribution of the $s-d$ exchange interaction, J^{weak}_{sd}, the contribution of the assisted tunneling due to the existence of localized states (the potential scattering with the impurities), J^{weak}_{imp}, and the contribution of the interference between the former two, $J^{weak}_{interference}$. Since J^{weak}_{sd} and J^{weak}_{imp} are odd functions to bias V, they can be combined to J^{weak}_{odd}. The corresponding differential conductance, $G^{weak}_{even} \equiv \partial J^{weak}_{odd}/\partial V$, is an even function to V. G^{weak}_{even} is obtained as

$$G^{weak}_{even} = G^{(2)} + G^{(3)}, \tag{2.116}$$

$$G^{(2)} = \frac{4\pi e^2}{\hbar}\rho^a(0)\rho^b(0)\{T^2 + N_a[2TT_a + T_a^2 + S(S+1)T_{Ja}^2$$

$$
\begin{aligned}
& +T_{Ja}^2\frac{\langle M\rangle}{2}\times(\tanh\frac{eV+\Delta}{2k_BT}+\tanh\frac{\Delta-eV}{2k_BT})]\}, && (2.117)\\
G^{(3)} &= G_1^{(3)}+G_2^{(3)}+G_3^{(3)}, && (2.118)\\
G_1^{(3)} &= C\{1-\frac{\langle M^2\rangle}{S(S+1)}+\frac{\langle M\rangle}{2S(S+1)} \\
& \times(\tanh\frac{\Delta-eV}{2k_BT})+\tanh\frac{\Delta+eV}{2k_BT}\}\times F(eV), && (2.119)\\
G_2^{(3)} &= \frac{C}{2}\{1+\frac{\langle M^2\rangle}{S(S+1)}+\frac{\langle M\rangle}{S(S+1)}\tanh\frac{\Delta+eV}{2k_BT}\} \\
& \times F(eV+\Delta), && (2.120)\\
G_3^{(3)} &= \frac{C}{2}\{1+\frac{\langle M^2\rangle}{S(S+1)}+\frac{\langle M\rangle}{S(S+1)}\tanh\frac{\Delta-eV}{2k_BT}\} \\
& \times F(eV-\Delta), && (2.121)
\end{aligned}
$$

where

$$C=-\frac{8\pi e^2}{\hbar}S(S+1)\rho^a(\epsilon_F)\rho^b(\epsilon_F)N_aT_{Ja}^2J_aF(eV). \qquad (2.122)$$

The conductance G_{even}^{weak} can be reduced to

$$G_{even}^{weak}=G_1(V)+G_2(V)+G_3(V), \qquad (2.123)$$

where

$$
\begin{aligned}
G_n(V) &= \int_{-\infty}^{\infty}g_n(\omega)\frac{\partial f(\omega-V)}{\partial\omega}d\omega, && (2.124)\\
g_1 &= a_1, && (2.125)\\
g_2 &= a_2[S(S+1)+\frac{\langle M\rangle}{2}(\tanh\frac{\omega+\Delta}{2k_BT}+\tanh\frac{\Delta-\omega}{2k_BT})], && (2.126)\\
g_3 &= a_3(g_{31}+g_{32}+g_{33}), && (2.127)\\
g_{31} &= [S(S+1)-\langle M^2\rangle \\
& +\frac{1}{2}\langle M\rangle\times(\tanh\frac{\omega+\Delta}{2k_BT}+\tanh\frac{\Delta-\omega}{2k_BT})]F(\omega), && (2.128)\\
g_{32} &= \frac{1}{2}[S(S+1)+\langle M^2\rangle+\langle M\rangle\tanh\frac{\omega+\Delta}{2k_BT}]F(\omega+\Delta), && (2.129)
\end{aligned}
$$

$$g_{33} = \frac{1}{2}[S(S+1) + \langle M^2 \rangle + \langle M \rangle \tanh \frac{-\omega + \Delta}{2k_BT}]F(\omega - \Delta). \quad (2.130)$$

where

$$F(\omega) = \int_{-E_0}^{E_0} \frac{f(E) - \frac{1}{2}}{\omega - E} dE, \quad (2.131)$$

E_0 is a cutoff parameter used to prevent well-known ultraviolate divergence difficulties. And

$$\begin{aligned} \langle M \rangle &= \sum_{M=-S}^{M=S} P_M M \\ &= \begin{cases} 0, \text{ if } H = 0 \\ \frac{1}{2}\coth(\frac{\Delta}{2k_BT}) - (S+\frac{1}{2})\coth[(S+\frac{1}{2})\frac{\Delta}{k_BT}], \text{ if } H \neq 0 \end{cases} \end{aligned} \quad (2.132)$$

$$\begin{aligned} \langle M^2 \rangle &= \sum_{M=-S}^{M=S} P_M M^2 \\ &= \begin{cases} \frac{1}{3}S(S+1), \text{ if } H = 0 \\ \langle M \rangle^2 - (S+\frac{1}{2})^2 \mathrm{csch}^2[(S+\frac{1}{2})\frac{\Delta}{k_BT}] + \frac{1}{4}\mathrm{csch}^2(\frac{\Delta}{2k_BT}), \text{ if } H \neq 0 \end{cases} \end{aligned} \quad (2.133)$$

In the zero magnetic field, we substitute $\Delta = 0$, (2.132), and (2.133) in (2.126) to (2.130), and get

$$g_2 = a_2 S(S+1), \quad (2.134)$$

$$g_{31} = [S(S+1) - \langle M^2 \rangle]F(\omega), \quad (2.135)$$

$$g_{32} = \frac{1}{2}[S(S+1) + \langle M^2 \rangle]F(\omega), \quad (2.136)$$

$$g_{33} = \frac{1}{2}[S(S+1) - \langle M^2 \rangle]F(\omega), \quad (2.137)$$

$$g_3 = a_3(g_{31} + g_{32} + g_{33}) = a_3 2S(S+1)F(\omega). \quad (2.138)$$

Therefore, if $H = 0$,

$$G_1(V) = \int_{-\infty}^{\infty} a_1 \frac{\partial f(\omega - eV)}{\partial \omega} d\omega = -a_1, \quad (2.139)$$

$$
\begin{aligned}
G_2(V) &= \int_{-\infty}^{\infty} a_2 S(S+1)\frac{\partial f(\omega - eV)}{\partial \omega} d\omega = -a_2 S(S+1), &(2.140)\\
G_3(V) &= \int_{-\infty}^{\infty} a_3 2S(S+1)F(\omega)\frac{\partial f(\omega - eV)}{\partial \omega} d\omega \\
&= 2a_3 S(S+1)\int_{-\infty}^{\infty} F(\omega)\frac{\partial f(\omega - eV)}{\partial \omega} d\omega, &(2.141)
\end{aligned}
$$

where

$$
F(\omega) = \int_{-E_0}^{E_0} \frac{f(E)-\frac{1}{2}}{\omega - E} dE = \frac{1}{2}\int_{-E_0}^{E_0} \frac{1-2f(\epsilon')}{\epsilon' - \omega} d\epsilon' = \frac{1}{2}\int_{-E_0}^{E_0} \frac{\tanh(\frac{\epsilon'}{2k_BT})}{\epsilon' - \omega} d\epsilon'. \tag{2.142}
$$

Therefor

$$
G_3(V) = a_3 S(S+1)\int_{-\infty}^{\infty}[\int_{-E_0}^{E_0} \frac{\tanh(\frac{\epsilon'}{2k_BT})}{\epsilon' - \omega} d\epsilon']\frac{\partial f(\omega - eV)}{\partial \omega} d\omega. \tag{2.143}
$$

And then we can get

$$
\begin{aligned}
G^{weak}_{even}(V) &= G_1(V) + G_2(V) + G_3(V) \\
&= -a_1 - a_2 S(S+1) \\
&\quad + a_3 S(S+1)\int_{-\infty}^{\infty}[\int_{-E_0}^{E_0} \frac{\tanh(\frac{\epsilon'}{2k_BT})}{\epsilon' - \omega} d\epsilon']\frac{\partial f(\omega - eV)}{\partial \omega} d\omega \\
&= A - B\int_{-\infty}^{\infty}[\int_{-E_0}^{E_0} \frac{\tanh(\frac{\epsilon'}{2k_BT})}{\epsilon' - \omega} d\epsilon']\frac{\partial f(\omega - eV)}{\partial \omega} d\omega. &(2.144)
\end{aligned}
$$

where $A = -a_1 - a_2 S(S+1)$, and $B = a_3 S(S+1)$. The proof that $G^{weak}_{even}(V)$ is an even function is left in Appendix A.

After deriving the even conductance, G^{weak}_{even}, in the weak coupling regime, we turn to the interference term. The tunneling current contributed from the interference effect, $J^{weak}_{interference}$, was calculated as [3]:

$$
\begin{aligned}
J^{weak}_{interference}(V) &= \frac{6\pi e T_a T_J}{\hbar}\int_{-\infty}^{\infty}\{[f(\omega) - f(\omega + eV)]\rho^b(\omega + eV)\rho^a(\omega) \\
&\quad \times \tanh\frac{\omega}{2k_BT}(1 - 6J\rho^a \ln|\frac{\omega}{D}|)\pi^2(J\rho^a)^2\} d\omega. &(2.145)
\end{aligned}
$$

$J^{weak}_{interference}$ is an even function to V, and therefore the corresponding differential conductance, G^{weak}_{odd}, is an odd function to V, and can be obtained as:

$$\begin{aligned} G^{weak}_{odd}(V) &\equiv \frac{\partial J^{weak}_{interference}}{\partial V} \\ &= \frac{6\pi^3 e^2 T_a T_J}{\hbar}\rho^b(0)\rho^a(0)(J\rho^a)^2 \int_{-\infty}^{\infty}\{\frac{-\partial f(\omega+eV)}{\partial(eV)} \\ &\qquad \times \tanh\frac{\omega}{2k_BT}(1-6J\rho^a \ln|\frac{\omega}{E_0}|)\}d\omega \\ &= \alpha\int_{-\infty}^{\infty}\frac{-\partial f(\omega+eV)}{\partial(eV)}\tanh\frac{\omega}{2k_BT}(1-6J\rho^a \ln|\frac{\omega}{E_0}|)d\omega, \end{aligned} \tag{2.146}$$

where

$$\alpha = \frac{6\pi^3 e^2 T_a T_J}{\hbar}\rho^b(0)\rho^a(0)(J\rho^a)^2. \tag{2.147}$$

2.3.2 Strong Coupling Regime

In the low temperatures limit, the system in in the strong coupling regime and the perturbation approach used above in not applicative. Appelbaum [3] utilized the self-consistent solution to the bulk Kondo effect, which was given by Nagaoka [8], to calculate the tunneling current in the strong coupling regime. Similar to the weak coupling case, the tunneling current contains three parts, the contribution of the $s-d$ exchange interaction, J^{strong}_{sd}, the contribution of the assisted tunneling due to the existence of localized states (the potential scattering with the impurities), J^{strong}_{imp}, and the contribution of the interference between the former two, $J^{strong}_{interference}$. They can be expressed as:

$$\begin{aligned} J^{strong}_{sd}(V) &= \frac{4eT_J^2}{\hbar\pi(J\rho^a)^2}\int_{-\infty}^{\infty}\{[f(\omega)-f(\omega+eV)] \\ &\qquad \times \rho^b(\omega+eV)\rho^a(\omega)\frac{\Delta^2}{\Delta^2+\omega^2}\}d\omega, \end{aligned} \tag{2.148}$$

$$J_{imp}^{strong}(V) = \frac{4\pi e T_a^2}{\hbar}\int_{-\infty}^{\infty}\{[f(\omega)-f(\omega+eV)] \times \rho^b(\omega+eV)\rho^a(\omega)\frac{\omega^2}{\Delta^2+\omega^2}\}d\omega, \tag{2.149}$$

$$J_{interference}^{strong}(V) = \frac{8eT_aT_J}{\hbar|J\rho^a|}\int_{-\infty}^{\infty}\{[f(\omega)-f(\omega+eV)] \times \rho^b(\omega+eV)\rho^a(\omega)\frac{\Delta\omega}{\Delta^2+\omega^2}\}d\omega, \tag{2.150}$$

respectively. Here $\Delta = k_BT_K$.

The corresponding differential conductance can be obtained as:

$$\begin{aligned} G_{sd}^{strong}(V) &= \frac{4e^2T_J^2}{\hbar\pi(J\rho^a)^2}\rho^b(0)\rho^a(0)\int_{-\infty}^{\infty}[\frac{-\partial f(\omega+eV)}{\partial(eV)} \times \frac{\Delta^2}{\Delta^2+\omega^2}]d\omega \\ &= \frac{4e^2T_J^2}{\hbar\pi(J\rho^a)^2}\rho^b(0)\rho^a(0)\frac{\Delta^2}{\Delta^2+(eV)^2}, \end{aligned} \tag{2.151}$$

$$\begin{aligned} G_{imp}^{strong}(V) &= \frac{4\pi e^2T_a^2}{\hbar}\rho^b(0)\rho^a(0)\int_{-\infty}^{\infty}[\frac{-\partial f(\omega+eV)}{\partial(eV)} \times \frac{\omega^2}{\Delta^2+\omega^2}]d\omega \\ &= \frac{4\pi e^2T_a^2}{\hbar}\rho^b(0)\rho^a(0)\frac{(eV)^2}{\Delta^2+(eV)^2}, \end{aligned} \tag{2.152}$$

$$G_{interference}^{strong}(V) = \frac{8e^2T_aT_J}{\hbar|J\rho^a|}\rho^b(0)\rho^a(0)\int_{-\infty}^{\infty}[\frac{-\partial f(\omega+eV)}{\partial(eV)} \times \frac{\Delta\omega}{\Delta^2+\omega^2}]d\omega \tag{2.153}$$

$$= \frac{-8e^2T_aT_J}{\hbar|J\rho^a|}\rho^b(0)\rho^a(0)\frac{\Delta eV}{\Delta^2+(eV)^2}. \tag{2.154}$$

It is obvious from (2.152), (2.153) and (2.154) that G_{sd}^{strong} and G_{imp}^{strong} symmetric to V while $G_{interference}^{strong}$ is asymmetric. Therefore G_{sd}^{strong} and G_{imp}^{strong} can be combined to an even function as

$$\begin{aligned}
G_{even}^{strong}(V) &= G_{sd}^{strong}(V) + G_{imp}^{strong}(V) \\
&= \frac{a_1 \times (eV)^2 + a_2 \times \Delta^2}{(eV)^2 + \Delta^2}, \qquad (2.155)
\end{aligned}$$

where

$$\begin{aligned}
a_1 &= \frac{4\pi e^2}{\hbar} T_a^2 \rho^a(0)\rho^b(0), \\
a_2 &= \frac{4e^2}{\hbar\pi(J\rho^a)^2} T_J^2 \rho^a(0)\rho^b(0), \\
\Delta &= k_B T_K. \qquad (2.156)
\end{aligned}$$