Kondo effect

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1. Introduction

Since 1930's, it has been well-known that at very low temperatures the metals with magnetic impurities exhibits an anomaly in the temperature dependence of their electrical resistivity; instead of the generally known decrease of resistivity with lowering temperature, it increases with decreasing temperatures. This effect is named as the Kondo effect, after Kondo (Jun). In 1964, Kondo has succeeded for the first time in explaining using the perturbation method, with scattering of electrons on magnetic impurities taken into account. In 1981, the exact solution of the Kondo problem was obtained later, by N. Andrei and Paul Wiegmann, separately. Note that the methods and ideas (by Abrikosov, Nozieres ,Wilson, Yosida, and et al.), which were needed to explain the Kondo effect, had played the most important role in studying the fundamental phenomenon of the electron localization- a part of modern physics and physical application.

In this note I do not intend to present various kinds of theories on the Kondo effect. It is beyond my ability. I am interested in the experimental results. I have been doing research on the spin glasses, experimentally using the techniques of aging dynamics. When one starts to read typical books on spin glass (such as Mydosh) as beginner, one may encounter excellent experimental data on canonical spin glasses (for example, Cu host diluted with magnetic impurity such as Mn or Fe). When the concentration of the magnetic impurities is extremely dilute, it is found that the systems show Kondo effect. The magnetic impurity is isolated from other magnetic impurities. The antiferromagnetic interaction between the spin of the conduction electron and the spin of magnetic impurity (the s-d interaction) leads to the Kondo spin singlet. The magnetic moment will vanish below a characteristic temperature, Kondo temperature T_K. Although there is no phase transition at this temperature, the pair formation of antiparallel alignment of spins look so similar to the Cooper pair in BCS theory (spin singlet with orbital angular moment $L = 0$).

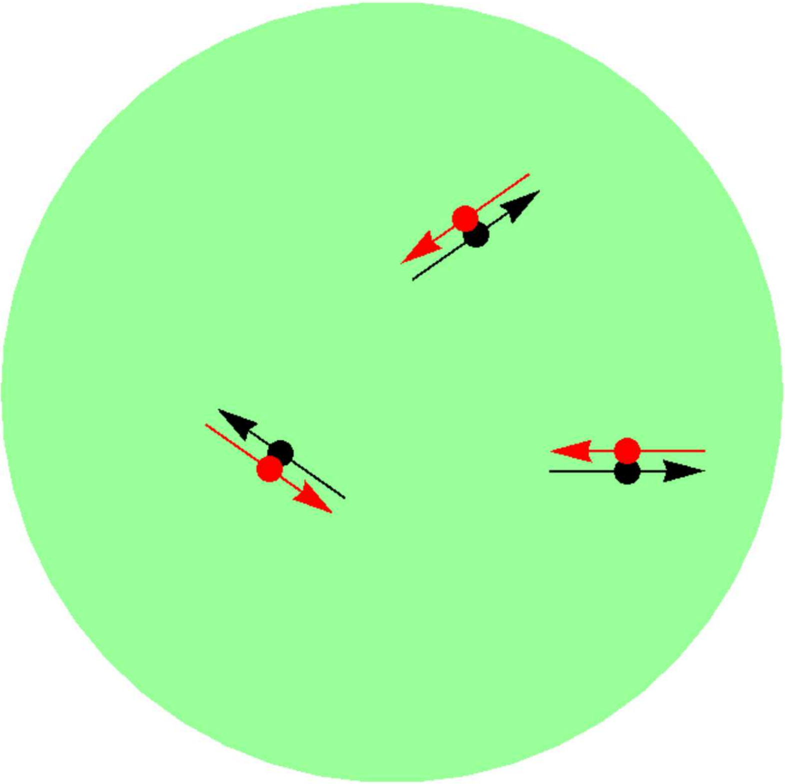


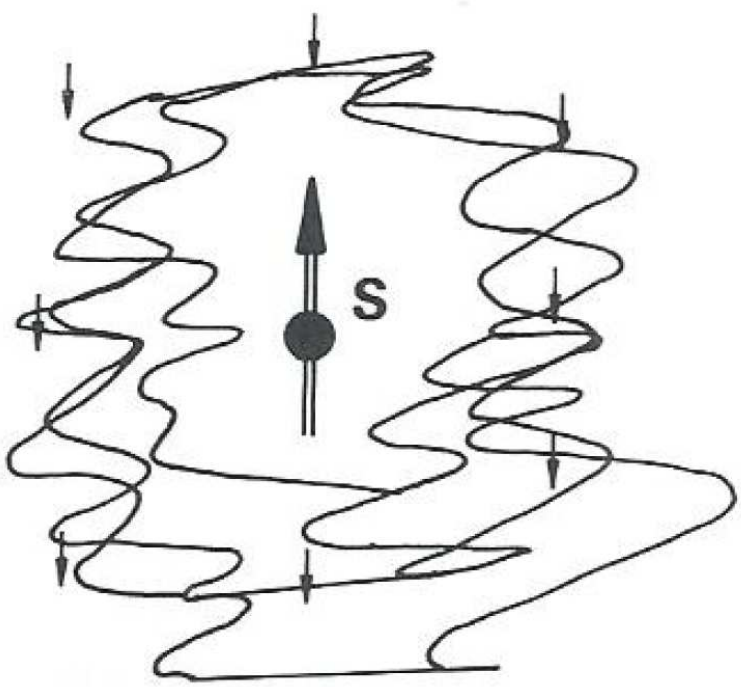
Fig. Isolated localized spins in a sea of conduction electrons, forming the singlet state of antiparallel alignment of conduction electron spin and the spin of magnetic impurity.

When the concentration of magnetic impurities is slightly increased, the system becomes a spin glass. The interaction between the magnetic impurities which is the so-called the RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction, plays an important role in spin glass behavior. The interaction between the magnetic impurities arises as a result of the interaction between the magnetic impurity and the conduction electrons. The sign of the interaction shows oscillatory change depending on the distance. The competition between the antiferromagnetic and ferromagnetic interactions leads to the fully frustrated nature of spin glass.

My first encounter with the Kondo effect occurred when I read the book of Thermoelectricity which was written by D.K.C. MacDonald. He showed a lot of excellent data of the thermoelectric power and electrical resistivity for canonical systems (for example, Cu host diluted with magnetic impurities). The temperature dependence of these two quantities are extremely sensitive to the concentration of magnetic impurities in the limit of dilute range. Even at the present stage, I am not sure whether the temperature dependence of the thermoelectric power as shown in the book of MacDonald, can be well explained.

2. Kondo effect and Jun Kondo

The **Kondo effect** is an unusual scattering mechanism of conduction electrons in a metal (such as noble metals) due to magnetic impurities9such as Mn, Fe), which contributes a term to the electrical resistivity that increases logarithmically with temperature as the temperature is decreased [as $\ln(T)$]. It is used to describe many-body scattering processes from impurities or ions which have low energy quantum mechanical degrees of freedom. In this sense it has become a key concept in condensed matter physics in understanding the behavior of metallic systems with strongly interacting electrons.



The Kondo effect is normally observed in very dilute magnetic alloys as a result of the interaction between the host conduction electrons and the magnetic impurity spins. In its ideal form, it is a single-impurity effect and leads to the rise of the electrical resistivity as the temperature is lowered down to zero temperature. It can be described by an effective interaction which increases with decreasing temperature and finally leads to a single state formed by a single impurity spin and the spins of the surrounding conduction electrons (Kondo, Nozieres, Wilson). At larger concentrations, the impurity-spin interaction becomes significant and leads to a partial destruction of single state. The impurities again become magnetic, leading to a spin glass for typically, a few percent magnetic impurities.

Fig. Picture of Prof. Jun Kondo
http://www.aist.go.jp/aist_j/information/emeritus_advisor/index.html

3. Experimental results

In 1934a resistance minimum was observed in gold as a function of temperature (de Haas, de Boer and van den Berg 1934), indicating that there must be some additional scattering mechanism giving an anomalous contribution to the resistivity--- one which increases in strength as the temperature is lowered. Other examples of metals showing a resistance minimum were later observed, and its origin was a longstanding puzzle for about 30 years. In the early 1960s it was recognized that the resistance minima are associated with magnetic impurities in the metallic host --- a magnetic impurity being one which has a local magnetic moment due to the spin of unpaired electrons in its atomic-like d or f shell. A carefully studied example showing the correlation between the resistance minima and the number of magnetic impurities is that of iron impurities in gold (van den Berg, 1964). In his book entitled Thermoelectricity, An Introduction to the Principles (first published in 1961 from John & Wiley), MacDonald (D.K.C.) showed various kinds of experimental results of electrical resistivity and thermoelectric power for noble metals (Au, Cu) diluted with magnetic impurities such as Mn and Fe. The electrical resistivity of Cu diluted with Mn or Fe clearly shows a local minimum at low temperatures. The temperature dependence of the thermoelectric power at low T is extremely sensitive to the amount of the magnetic impurities; Au diluted with Mn.

(a) Electrical resistivity

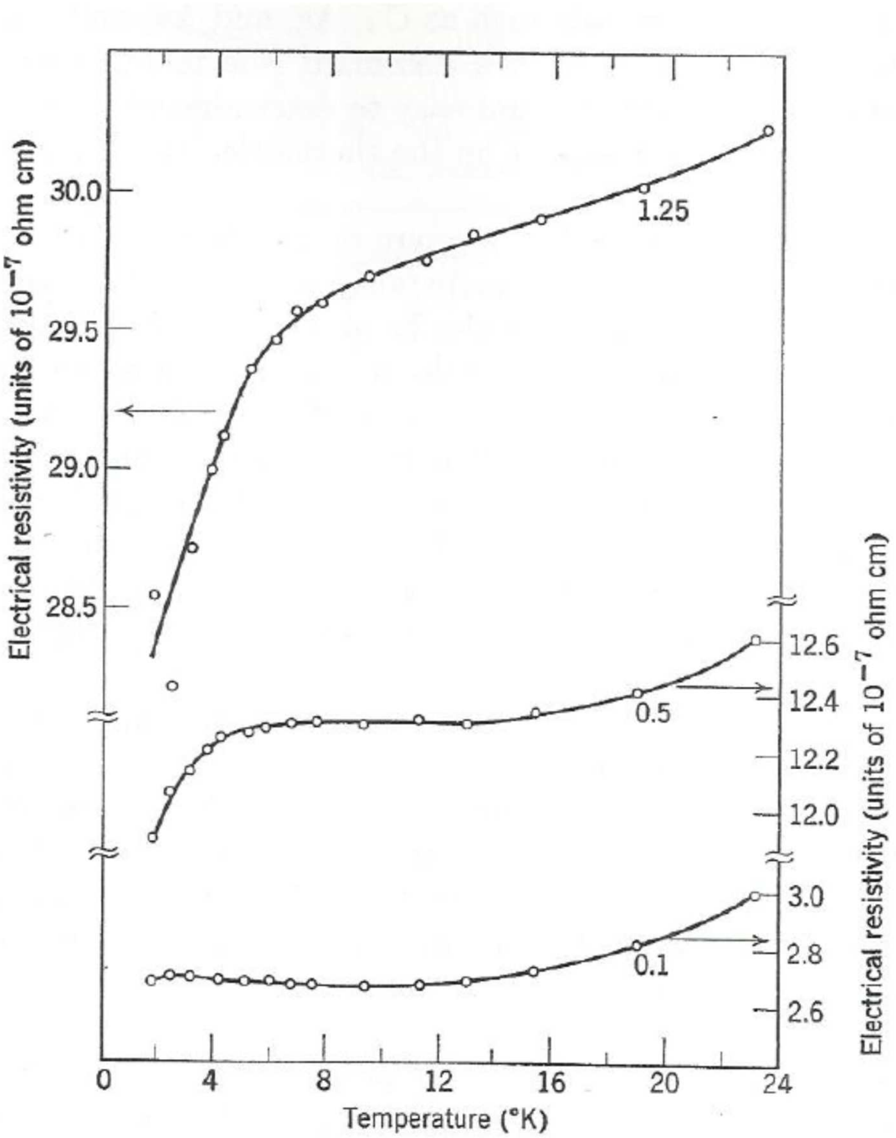


Fig. Electrical resistivity of Au with Mn as solute. The nominal atomic concentration of Mn is indicated on each curve. (**D.K.C. MacDonald, Thermoelectricity, Dover, 2006**).

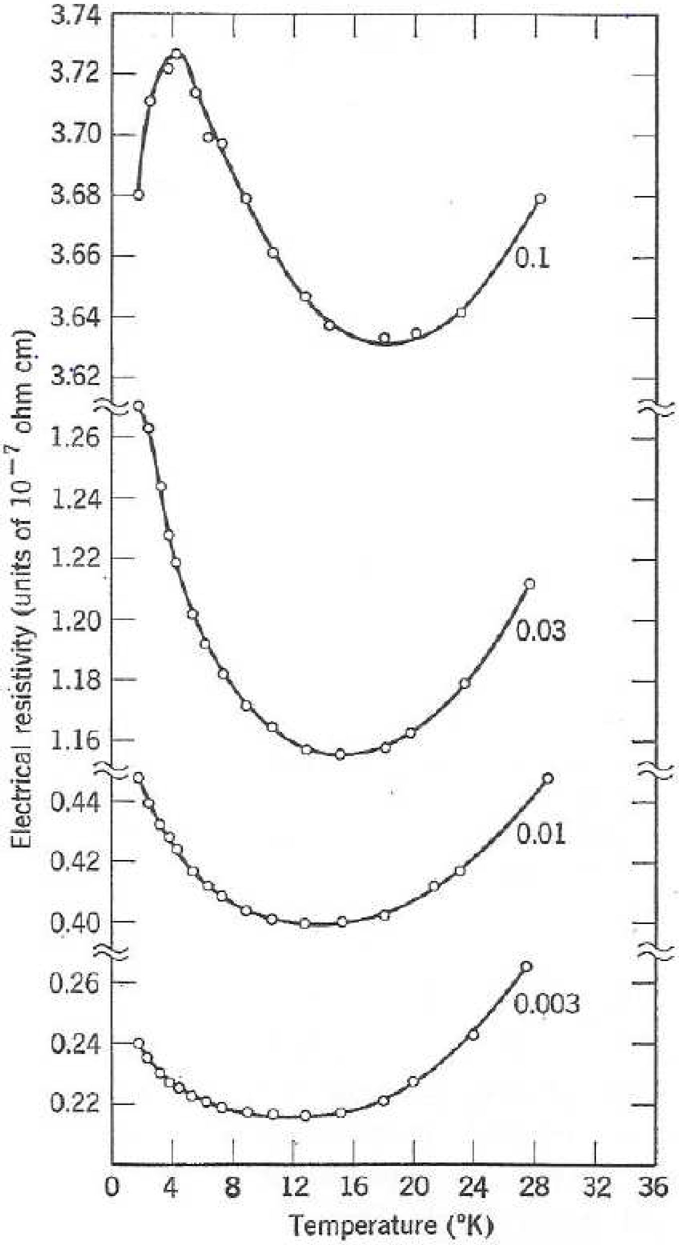


Fig. Electrical resistivity of Cu with Mn as solute. The nominal atomic concentration of Mn is indicated on each curve. (**D.K.C. MacDonald, Thermoelectricity, Dover, 2006**).

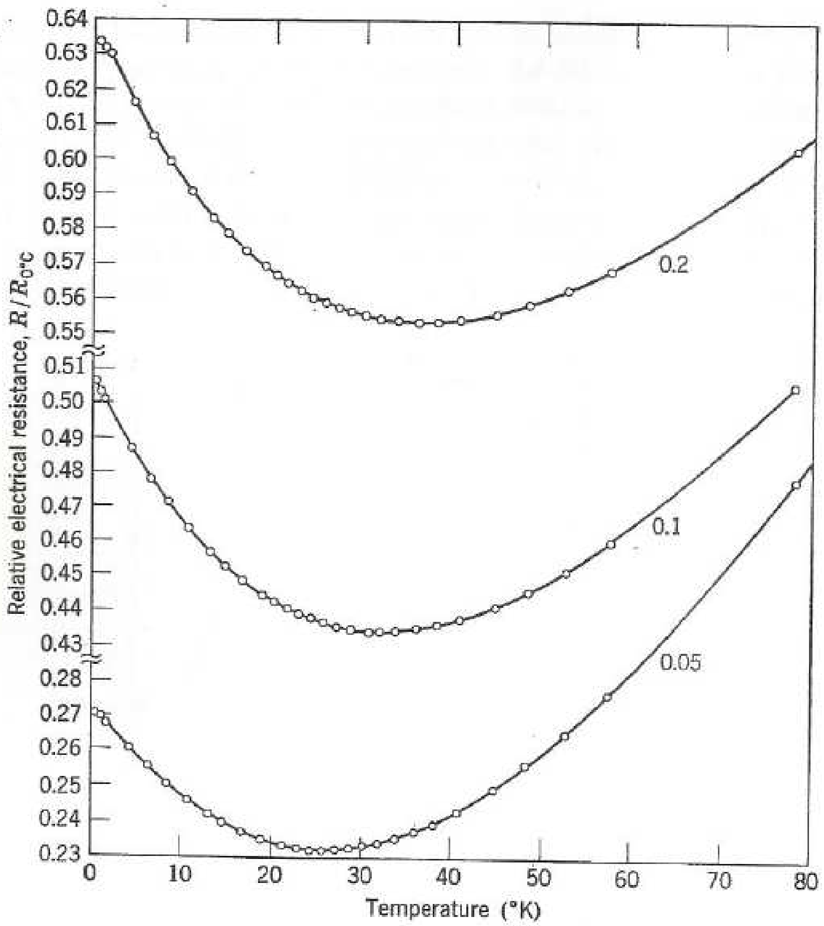


Fig. Electrical resistivity of Cu with Fe as solute. The nominal atomic concentration of Fe is indicated on each curve. (**D.K.C. MacDonald, Thermoelectricity, Dover, 2006**).

(b) Thermoelectric power

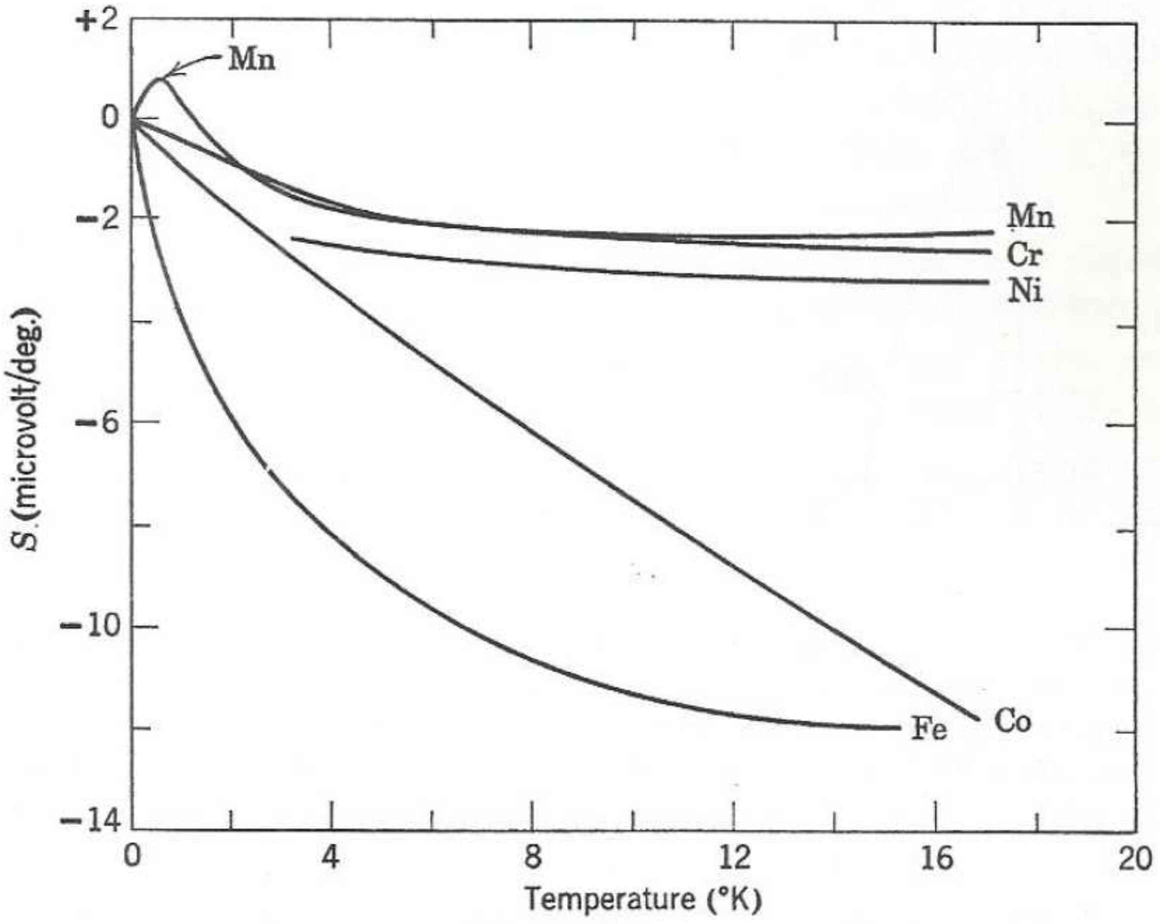


Fig. Thermoelectric power at low T of Au alloys with a range of transition metals as solutes. Each alloy has a concentration of 0.2 nominal atomic percent as solute of the transition metal indicated on the curve. (**D.K.C. MacDonald, Thermoelectricity, Dover, 2006**)

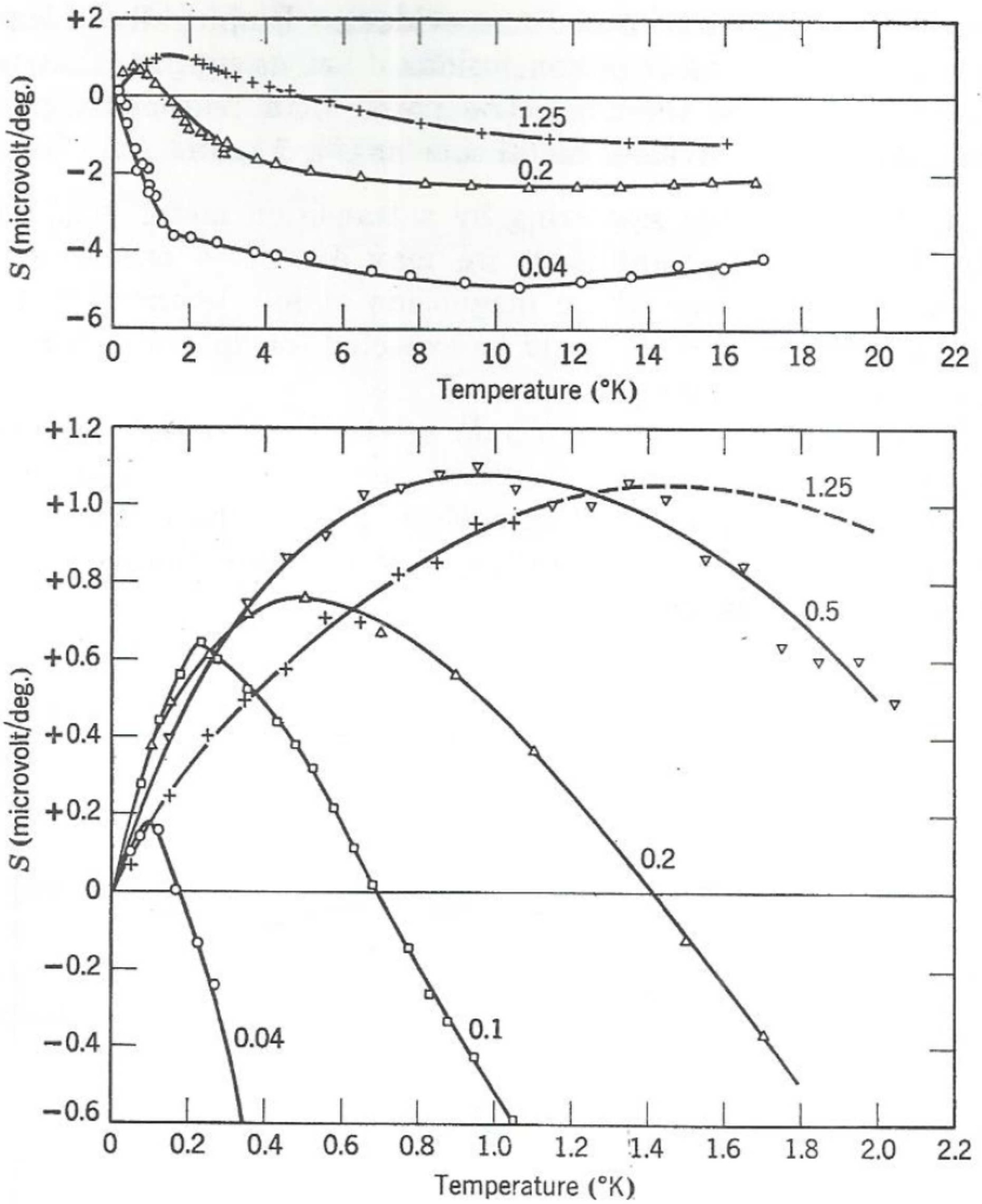


Fig. Thermoelectric power at low *T* of Au alloys with Mn as solutes. The nominal atomic concentration of Mn is indicated on each curve. The behavior of the most dilute alloys below 1 K is particularly striking. (**D.K.C. MacDonald, Thermoelectricity, Dover, 2006**).

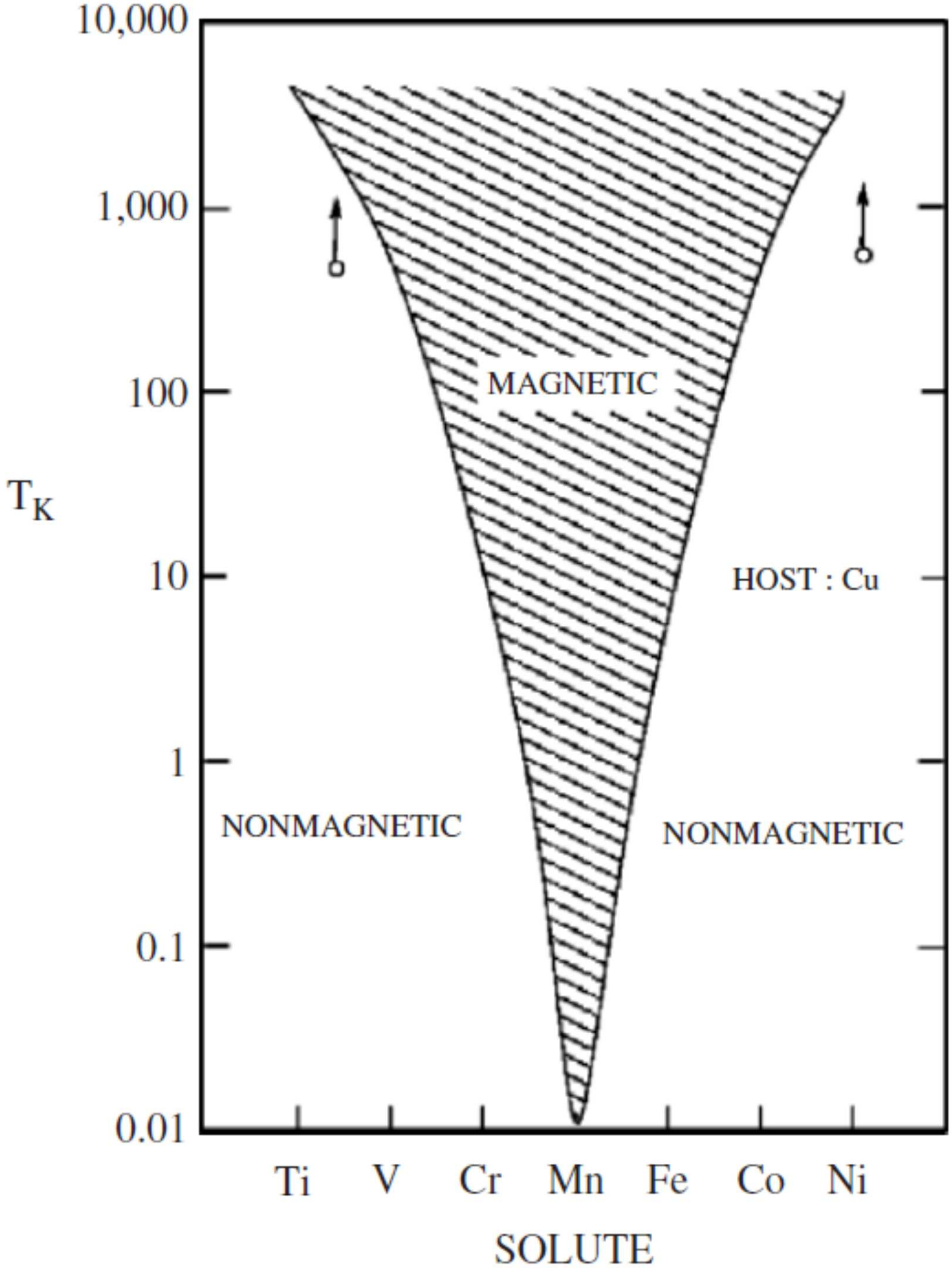


Fig. Variation of the Kondo temperature for the 3d transition metals in Cu host.

4. Spin glass region for canonical systems

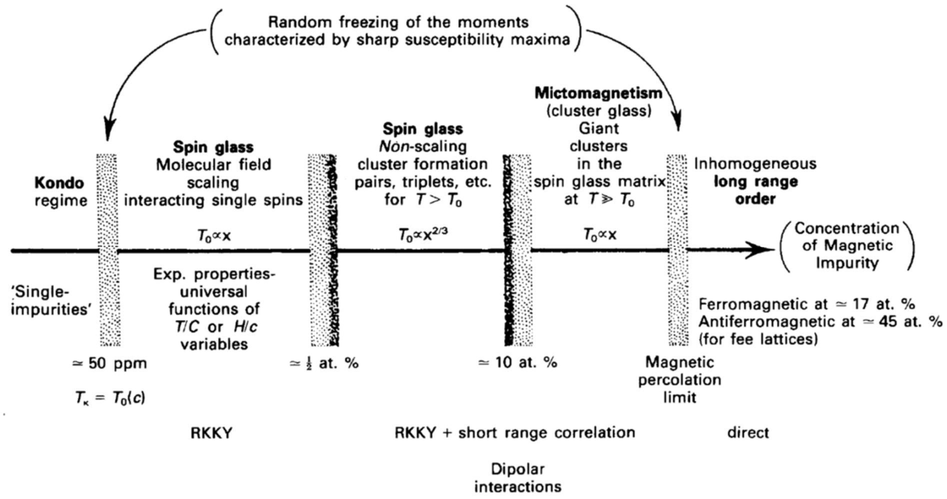


Fig. Various concentration regimes for a canonical spin glass (such as host Cu diluted with Mn) illustrating the different types of magnetic behavior which occur. (**J.A. Mydosh, Spin Glass, Taylor & Francis, London, 1993**)

The concentration is one of the most important factors in determining the magnetic state of the alloys. We show a schematic diagram for various concentration regime division. At the very dilute magnetic concentration (ppm) there are the isolated impurity-conduction electron coupling leading to the Kondo effect. This localized interaction (if $J<0$) causes a weakening or fluctuation of the magnetic moment, and below the Kondo temperature, the magnetic moment disappears and the impurity appears non-magnetic. Thus the Kondo effect prevents strong impurity-impurity interaction which are basic necessity of the spin glass. Up to a concentration of few thousand ppm (≈ 0.5 at. %), the RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction becomes significant to the interactions between the nearest neighbor magnetic impurities

$$J(r) = J_0 \frac{\cos(2k_F r + \phi)}{(2k_F r)^3},$$

at large distance r between two impurities, where k_F is the Fermi wave number, and J_0 is the exchange constant. The sign of the RKKY interaction depends on the separation distance between two magnetic impurities, because of its oscillatory nature. The competition between the ferromagnetic interaction and the antiferromagnetic interaction leads to the frustrated nature of spin order, so-called spin glass.

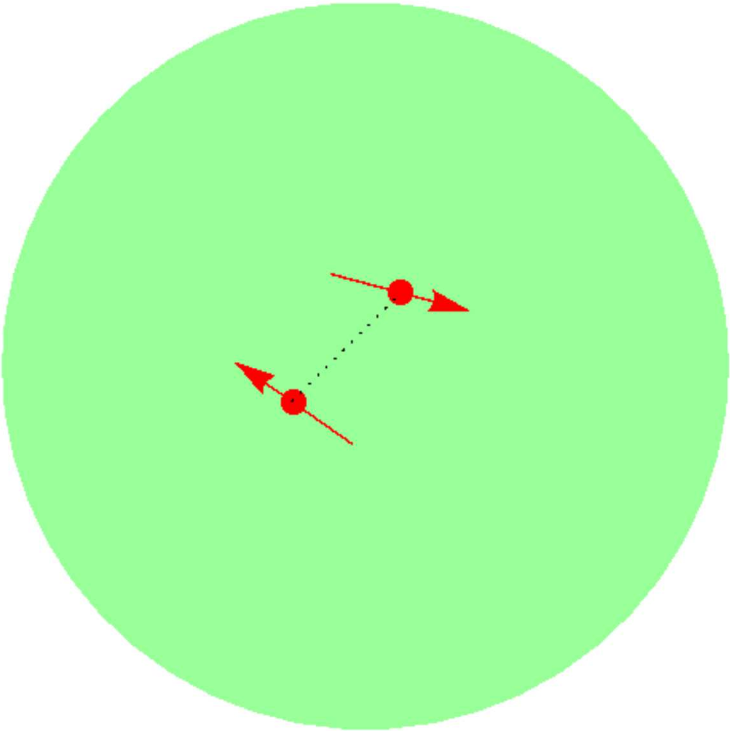


Fig. RKKY interaction between localized magnetic impurities. The red circle denotes the sea of conduction electrons.

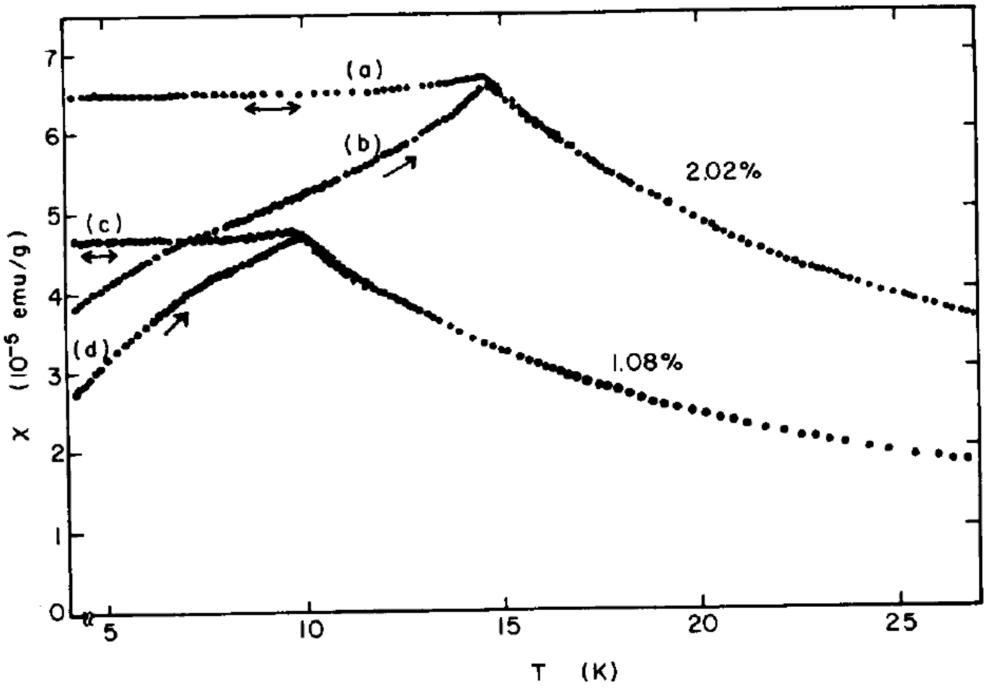


Fig. Field cooled (a, c) and zero-field (b, d) cooled magnetization for CuMn (1 and 2%) as a function of temperature The data shows clearly the characteristic features of spin glass behavior. (J.A. Mydosh, Spin Glasses, Taylor & Francis, 1993).

5. Kondo effect:minimum in resistivity vs temperature

In the 1930's it was found that the electrical resistivity of dilute magnetic alloys shows a minimum at a characteristic temperature. The resistivity decreases as the temperature decreases from the high temperature side. It shows a minimum value, and in turn increases with further decreasing temperature. These systems are noble metals such as Au, Ag, and Cu diluted with magnetic impurities such as Mn and Fe. Such temperature dependence is rather different from that for normal metals obeying the Bloch T^5 law at low temperatures. In 1964, Jun Kondo proposed a remarkable theory that explains the resistivity minimum. The interaction of conduction electrons with localized spins leads to the many body problem in electrons of metal. This effect is called the Kondo effect. The Kondo effect described the scattering of conduction electronic in a metal due to magnetic impurities.

The local minimum of the electrical resistivity arises from the competition between the following two contributions,

$$\begin{aligned}\rho &= \rho_{spin} + \rho_{Bloch} \\ &= c\rho_M(1+\frac{3zJ}{\varepsilon_F}\ln T) + aT^5 \\ &= c(\rho_0 - \rho_1 \ln T) + aT^5\end{aligned}$$

The first term is the spin-dependent contribution to the resistivity and the second term is the phonon contribution (Bloch T^5 law). J is the exchange energy, z is the number of nearest neighbors, c is the concentration, and ρ_M is a measure of the strength of the exchange scattering. The resistivity has a minimum at

$$\frac{d\rho}{dT} = 5aT^4 - c\rho_1 = 0$$

or

$$T_{\min} = \left(\frac{c\rho_1}{5a}\right)^{1/5}$$

The temperature at which the electrical resistivity takes a minimum, varies as one-fifth power of the concentration of the magnetic impurities, in agreement with experiment at least for Cu diluted with Fe.

6. Origin of exchange interaction

The Hamiltonian of the Anderson model can be described by

$$H_0 = \sum_{\boldsymbol{k},\sigma} \varepsilon_{\boldsymbol{k}} c_{\boldsymbol{k}\sigma}{}^{+} c_{\boldsymbol{k}\sigma} + \varepsilon_d \sum_{\sigma} n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow}$$

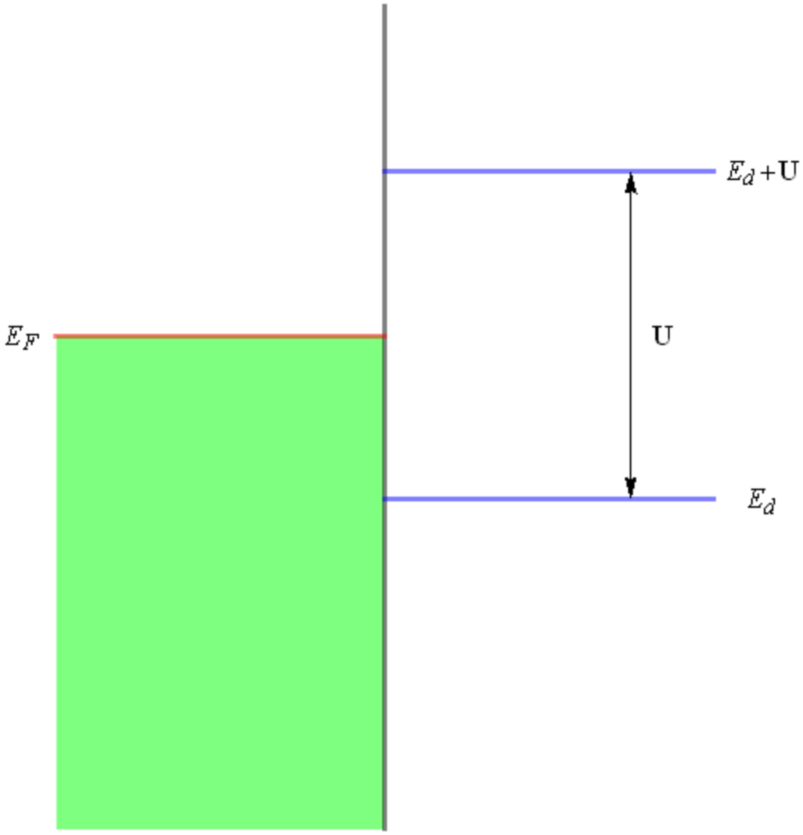
$$H' = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{k},\sigma} (V_{kd} c_{\boldsymbol{k}\sigma}{}^{+} d_\sigma + V_{dk} d_\sigma{}^{+} c_{\boldsymbol{k}\sigma}) \text{ (perturbation)}$$

where

$$n_{d\sigma} = d_\sigma{}^{+} d_\sigma \qquad (\sigma = \uparrow, \downarrow).$$

$$\{d_\sigma, d_\sigma{}^{+}\} = 1, \qquad \{c_{\boldsymbol{k}\sigma}, c_{\boldsymbol{k}'\sigma}{}^{+}\} = \delta_{\boldsymbol{k},\boldsymbol{k}'}$$

We now shoe that the s-d interaction can be derived from the Anderson model.



We consider the second-order process of *V* starting with

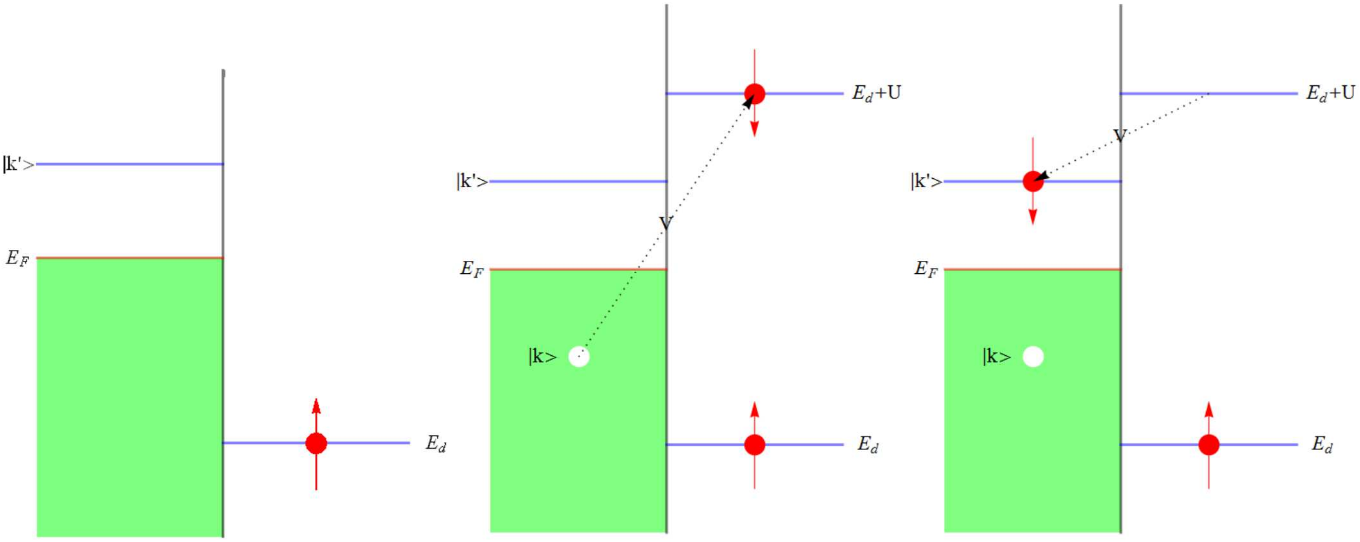
$$\left|\Phi_i\right\rangle = d_\uparrow{}^+\left|F\right\rangle .$$

where $\left|F\right\rangle$ is the state where the conduction electrons make up the Fermi sphere. Note that there is no d-electrons in the localized magnetic state. This state is degenerate with

$$\left|\Phi_i\right\rangle = d_\downarrow{}^+\left|F\right\rangle .$$

Process-1

$\boldsymbol{k}\downarrow$ enters $d_\downarrow$, and $d_\downarrow$ goes out to $\boldsymbol{k}'\downarrow$



$E_0 + E_d$ Initial state

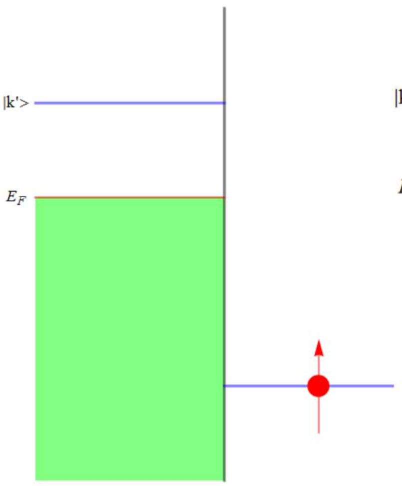
$E_0 - \varepsilon_k + E_d + E_d + U$ Intermediate state

$E_0 - \varepsilon_k + \varepsilon_{k'} + E_d$ Final state

$$V_1 = \frac{V_{k'd}V_{dk}}{\varepsilon_k - E_d - U} c_{k'\downarrow}{}^+ d_\downarrow d_\downarrow{}^+ c_{k\downarrow}$$

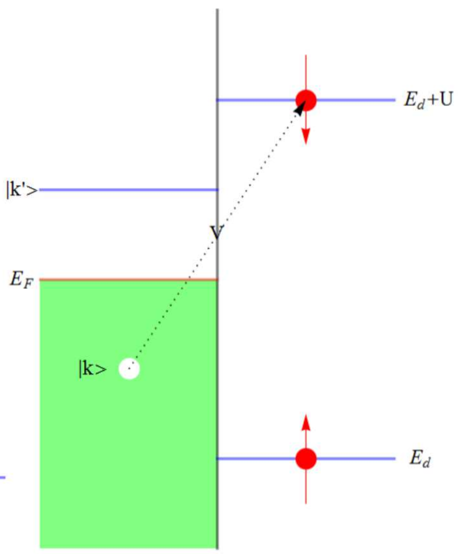
Process-2

$\boldsymbol{k}\downarrow$ enters $d_\downarrow$, and $d_\uparrow$ goes out to $\boldsymbol{k}'\uparrow$



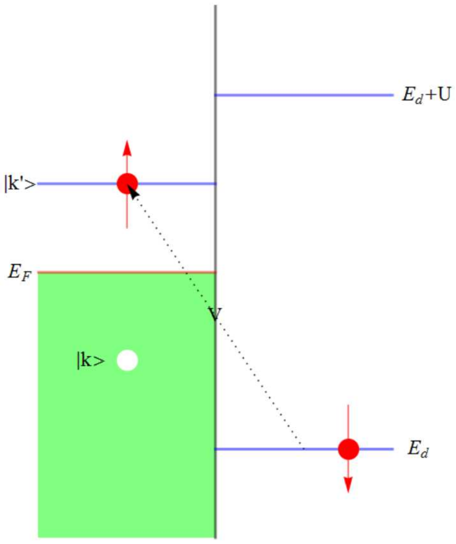
$E_0 + E_d$

Initial state



$E_0 - \varepsilon_k + E_d + E_d + U$

Intermediate state



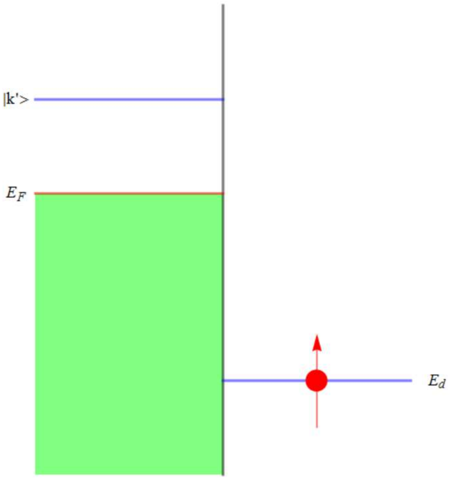
$E_0 - \varepsilon_k + \varepsilon_{k'} + E_d$

Final state

$$V_2 = \frac{V_{\boldsymbol{k}'d} V_{d\boldsymbol{k}}}{\varepsilon_{\boldsymbol{k}} - E_d - U} c_{\boldsymbol{k}'\uparrow}{}^{+} d_{\uparrow} d_{\downarrow}{}^{+} c_{\boldsymbol{k}\downarrow}$$

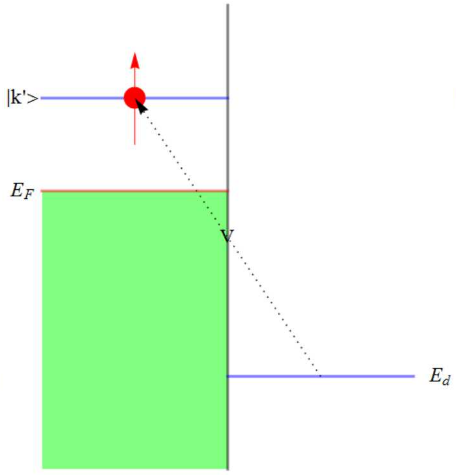
Process-3

$d_\uparrow$ enters $\boldsymbol{k}'\uparrow$, and $\boldsymbol{k}\uparrow$ goes out to $d_\uparrow$.



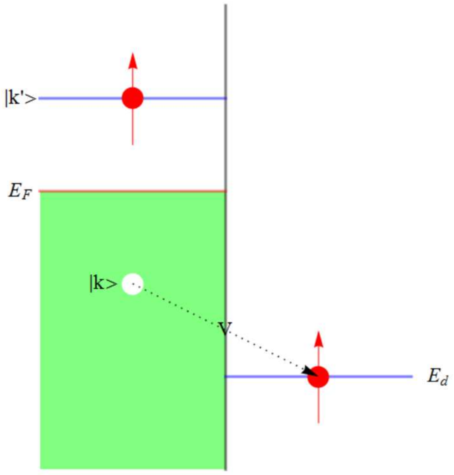
$E_0 + E_d$

Initial state



$E_0 + \varepsilon_{k'}$

Intermediate state



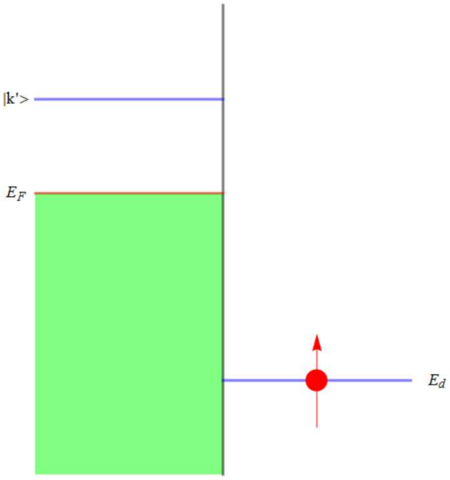
$E_0 - \varepsilon_k + \varepsilon_{k'} + E_d$

Final state

$$V_3 = \frac{V_{dk}V_{k'd}}{E_d - \varepsilon_{k'}} d_\uparrow{}^{+} c_{\boldsymbol{k}\uparrow} c_{\boldsymbol{k}'\uparrow}{}^{+} d_\uparrow$$

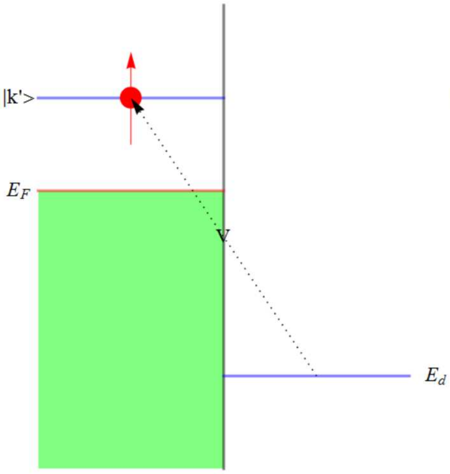
Process-4

$d_\uparrow$ enters $\boldsymbol{k}'\uparrow$, and $\boldsymbol{k}\downarrow$ goes out to $d_\downarrow$.



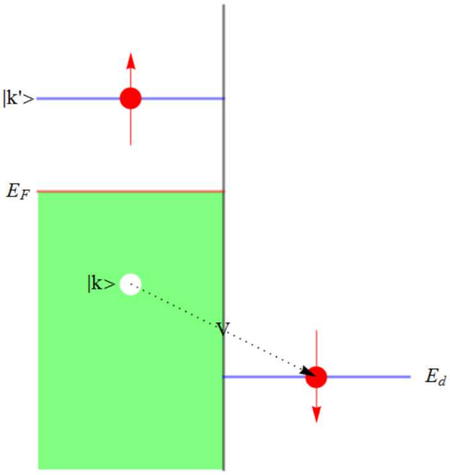
$E_0 + E_d$

Initial state



$E_0 + \varepsilon_{k'}$

Intermediate state



$E_0 - \varepsilon_k + \varepsilon_{k'} + E_d$

Final state

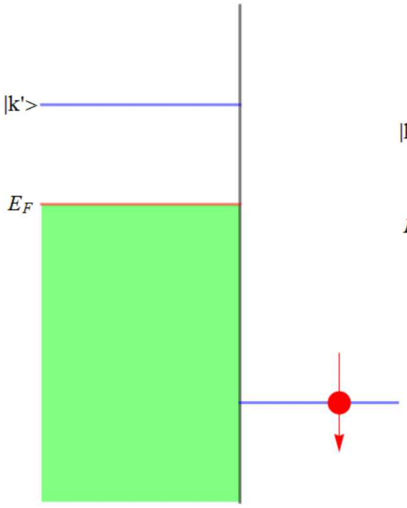
$$V_4 = \frac{V_{dk}V_{k'd}}{E_d - \varepsilon_{k'}} d_\downarrow{}^{+} c_{\boldsymbol{k}\downarrow} c_{\boldsymbol{k}'\uparrow}{}^{+} d_\uparrow$$

We consider the second-order process of V starting with

$$\left|\Phi_i\right\rangle = d_\downarrow{}^{+}\left|F\right\rangle.$$

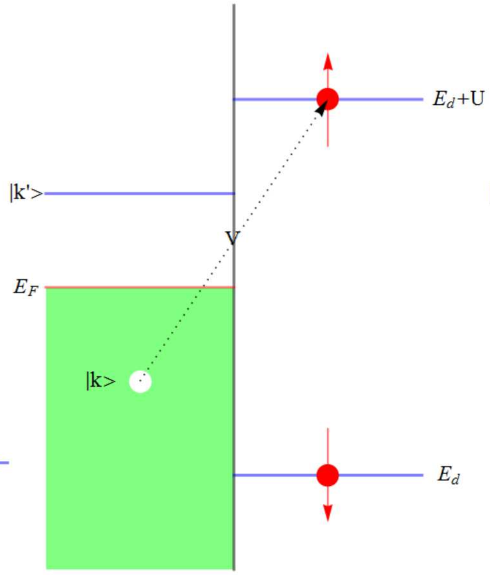
Process-5

$\boldsymbol{k}\uparrow$ enters $d_\uparrow$, and $d_\uparrow$ goes out to $\boldsymbol{k}'\uparrow$



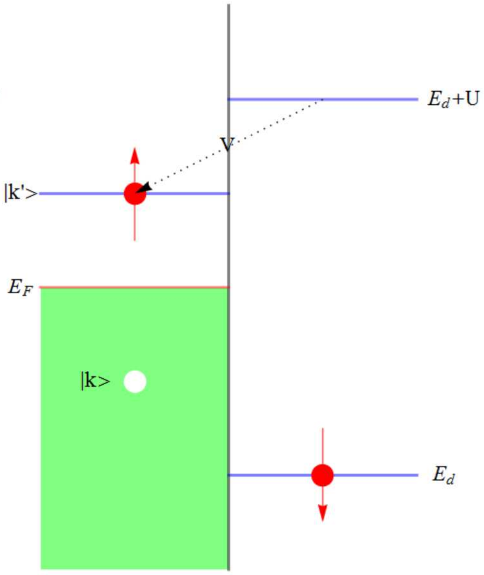
$E_0 + E_d$

Initial state



$E_0 - \varepsilon_k + E_d + E_d + U$

Intermediate state



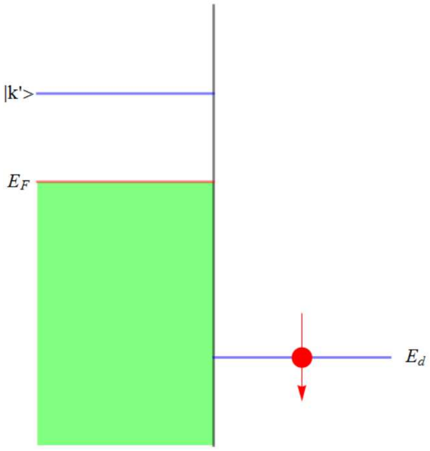
$E_0 - \varepsilon_k + \varepsilon_{k'} + E_d$

Final state

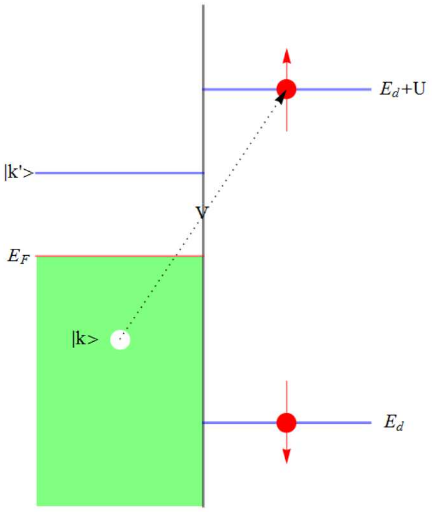
$$V_5 = \frac{V_{\boldsymbol{k}'d} V_{d\boldsymbol{k}}}{\varepsilon_{\boldsymbol{k}} - E_d - U} c_{\boldsymbol{k}'\uparrow}{}^{+} d_\uparrow d_\uparrow{}^{+} c_{\boldsymbol{k}\uparrow}$$

Process-6

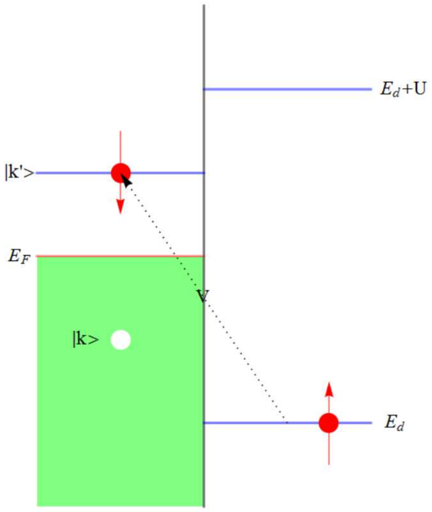
$\boldsymbol{k}\uparrow$ enters $d_\uparrow$, and $d_\downarrow$ goes out to $\boldsymbol{k}'\downarrow$



$E_0 + E_d$



$E_0 - \varepsilon_k + E_d + E_d + U$



$E_0 - \varepsilon_k + \varepsilon_{k'} + E_d$

Initial state

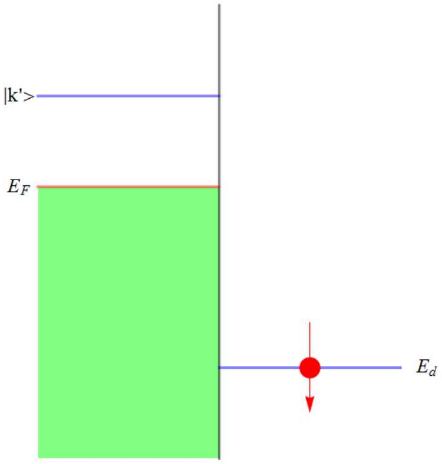
Intermediate state

Final state

$$V_6 = \frac{V_{\boldsymbol{k}'d}V_{d\boldsymbol{k}}}{\varepsilon_{\boldsymbol{k}} - E_d - U} c_{\boldsymbol{k}'\downarrow}{}^{+} d_\downarrow d_\uparrow{}^{+} c_{\boldsymbol{k}\uparrow}$$

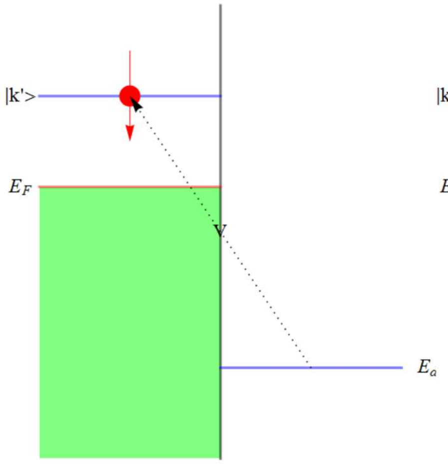
Process-7

$d_\downarrow$ enters $\boldsymbol{k}'\downarrow$, and $\boldsymbol{k}\downarrow$ goes out to $d_\downarrow$.



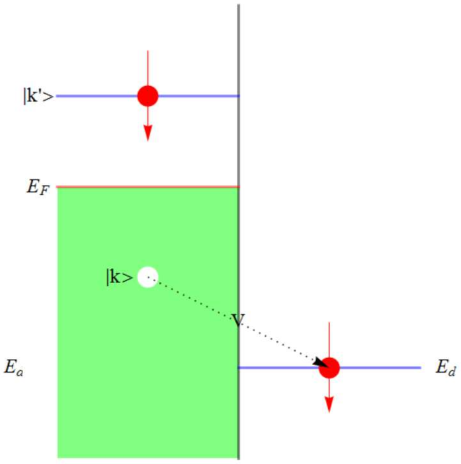
$E_0 + E_d$

Initial state



$E_0 + \varepsilon_{k'}$

Intermediate state



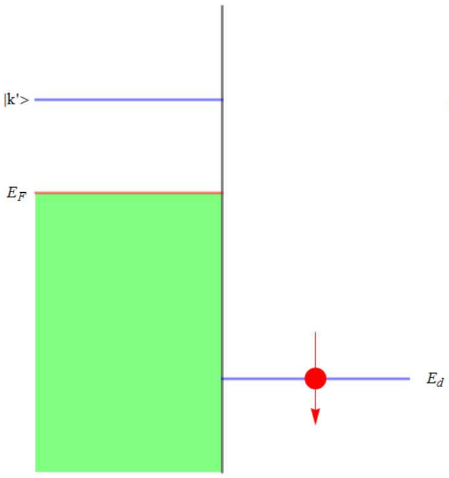
$E_0 - \varepsilon_k + \varepsilon_{k'} + E_d$

Final state

$$V_7 = \frac{V_{dk}V_{k'd}}{E_d - \varepsilon_{\boldsymbol{k}'}} d_\downarrow{}^{+} c_{k\downarrow} c_{k'\downarrow}{}^{+} d_\downarrow$$

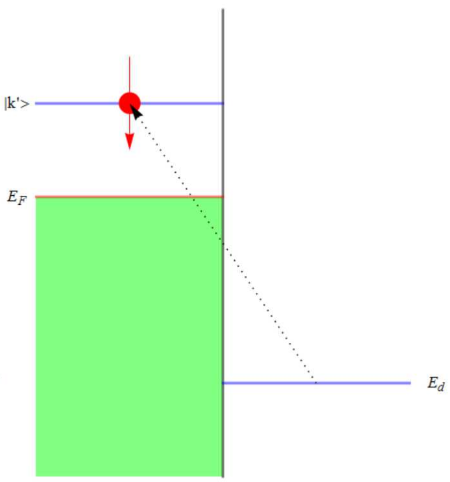
Process-8

$d_\downarrow$ enters $\boldsymbol{k}'\downarrow$, and $\boldsymbol{k}\uparrow$ goes out to $d_\uparrow$.



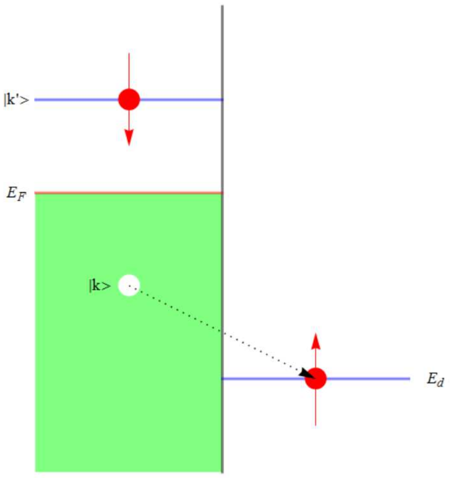
$E_0 + E_d$

Initial state



$E_0 + \varepsilon_{k'}$

Intermediate state



$E_0 - \varepsilon_k + \varepsilon_{k'} + E_d$

Final state

$$V_8 = \frac{V_{dk}V_{k'd}}{E_d - \varepsilon_{k'}} d_\uparrow^+ c_{k\uparrow} c_{k'\downarrow}^+ d_\downarrow$$

Adding to the all the processes above, we obtain the effective Hamiltonian,

$$\frac{V_{k'd}V_{dk}}{\varepsilon_k - E_d - U}(c_{k'\downarrow}^+ d_\downarrow d_\downarrow^+ c_{k\downarrow} + c_{k'\uparrow}^+ d_\uparrow d_\downarrow^+ c_{k\downarrow} + c_{k'\uparrow}^+ d_\uparrow d_\uparrow^+ c_{k\uparrow} + c_{k'\downarrow}^+ d_\downarrow d_\uparrow^+ c_{k\uparrow})$$
$$+ \frac{V_{dk}V_{k'd}}{E_d - \varepsilon_{k'}}(d_\uparrow^+ c_{k\uparrow} c_{k'\uparrow}^+ d_\uparrow + d_\downarrow^+ c_{k\downarrow} c_{k'\uparrow}^+ d_\uparrow + d_\downarrow^+ c_{k\downarrow} c_{k'\downarrow}^+ d_\downarrow + d_\uparrow^+ c_{k\uparrow} c_{k'\downarrow}^+ d_\downarrow)$$

Noting that

$$n_{d\uparrow} = d_\uparrow^+ d_\uparrow = \frac{1}{2} + S_z, \qquad n_{d\downarrow} = d_\downarrow^+ d_\downarrow = \frac{1}{2} - S_z$$

$$d_\uparrow^+ d_\uparrow + d_\downarrow^+ d_\downarrow = n_{d\uparrow} + n_{d\downarrow} = n_d = 1$$

$$S_z = \frac{1}{2}(d_\uparrow^+ d_\uparrow - d_\downarrow^+ d_\downarrow) = \frac{1}{2}(n_{d\uparrow} - n_{d\downarrow})$$

$$S_+ = d_\uparrow^+ d_\downarrow = -d_\downarrow d_\uparrow^+, \qquad S_- = d_\downarrow^+ d_\uparrow = -d_\uparrow d_\downarrow^+$$

we get

$$\begin{aligned}
& c_{\boldsymbol{k}'\downarrow}{}^{+}d_{\downarrow}d_{\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}+c_{\boldsymbol{k}'\uparrow}{}^{+}d_{\uparrow}d_{\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}+c_{\boldsymbol{k}'\uparrow}{}^{+}d_{\uparrow}d_{\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}+c_{\boldsymbol{k}'\downarrow}{}^{+}d_{\downarrow}d_{\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow} \\
&=c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}(1-n_{d\downarrow})-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\downarrow}d_{\downarrow}{}^{+}d_{\uparrow}+c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}(1-n_{d\uparrow})-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\uparrow}d_{\uparrow}{}^{+}d_{\downarrow} \\
&=c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}(1-n_{d\downarrow})-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\downarrow}S_{-}+c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}(1-n_{d\uparrow})-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\uparrow}S_{+} \\
&=(c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}+c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow})-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}n_{d\downarrow}-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\downarrow}S_{-}-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}n_{d\uparrow}-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\uparrow}S_{+}
\end{aligned}$$

for the coefficient of $\dfrac{V_{\boldsymbol{k}'d}V_{d\boldsymbol{k}}}{\varepsilon_{\boldsymbol{k}}-E_d-U}$

$$\begin{aligned}
& d_{\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}c_{\boldsymbol{k}'\uparrow}{}^{+}d_{\uparrow}+d_{\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}c_{\boldsymbol{k}'\uparrow}{}^{+}d_{\uparrow}+d_{\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}c_{\boldsymbol{k}'\downarrow}{}^{+}d_{\downarrow}+d_{\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}c_{\boldsymbol{k}'\downarrow}{}^{+}d_{\downarrow} \\
&=c_{\boldsymbol{k}\uparrow}c_{\boldsymbol{k}'\uparrow}{}^{+}d_{\uparrow}{}^{+}d_{\uparrow}+c_{\boldsymbol{k}\downarrow}c_{\boldsymbol{k}'\uparrow}{}^{+}d_{\downarrow}{}^{+}d_{\uparrow}+c_{\boldsymbol{k}\downarrow}c_{\boldsymbol{k}'\downarrow}{}^{+}d_{\downarrow}{}^{+}d_{\downarrow}+c_{\boldsymbol{k}\uparrow}c_{\boldsymbol{k}'\downarrow}{}^{+}d_{\uparrow}{}^{+}d_{\downarrow} \\
&=(\delta_{k,k'}-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow})n_{d\uparrow}-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\downarrow}S_{-}+(\delta_{k,k'}-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow})n_{d\downarrow}-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\uparrow}S_{+} \\
&=\delta_{k,k'}n_d-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}n_{d\uparrow}-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\downarrow}S_{-}-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}n_{d\downarrow}-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\uparrow}S_{+} \\
&=\delta_{k,k'}n_d-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}(1-n_{d\downarrow})-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\downarrow}S_{-}-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}(1-n_{d\uparrow})-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\uparrow}S_{+} \\
&=(\delta_{k,k'}n_d-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow})+(c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}n_{d\downarrow}+c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}n_{d\uparrow}-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\downarrow}S_{-}-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\uparrow}S_{+})
\end{aligned}$$

for the coefficient of $\dfrac{V_{d\boldsymbol{k}}V_{\boldsymbol{k}'d}}{E_d-\varepsilon_{\boldsymbol{k}'}}$.

The non-perturbed Hamiltonian is

$$\begin{aligned}
H^{(1)} &=\sum_{\boldsymbol{k},\boldsymbol{k}'}\Big[\frac{V_{\boldsymbol{k}'d}V_{d\boldsymbol{k}}}{E_d-\varepsilon_k}(c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}+c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}) \\
&\quad+\frac{V_{\boldsymbol{k}'d}V_{d\boldsymbol{k}}}{\varepsilon_k-E_d-U}(\delta_{k,k'}n_d-c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}-c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow})\Big] \\
&=\sum_{\boldsymbol{k},\boldsymbol{k}'}V_{\boldsymbol{k}'d}V_{d\boldsymbol{k}}\Big[\Big(\frac{1}{E_d-\varepsilon_k}-\frac{1}{\varepsilon_k-E_d-U}\Big)(c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow}+c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow}) \\
&\quad+\frac{1}{\varepsilon_k-E_d-U}\delta_{k,k'}\Big]
\end{aligned}$$

where $n_d=1$

The interaction Hamiltonian is

$$\begin{aligned}
H^{(2)} &= \sum_{\mathbf{k},\mathbf{k}'}[\frac{V_{\mathbf{k}'d}V_{d\mathbf{k}}}{E_d-\varepsilon_k}(-c_{\mathbf{k}\uparrow}{}^{+}c_{\mathbf{k}'\uparrow}n_{d\uparrow}-c_{\mathbf{k}\downarrow}{}^{+}c_{\mathbf{k}'\downarrow}n_{d\downarrow}-c_{\mathbf{k}\uparrow}{}^{+}c_{\mathbf{k}'\downarrow}S_{-}-c_{\mathbf{k}\downarrow}{}^{+}c_{\mathbf{k}'\uparrow}S_{+}) \\
&\quad+\frac{V_{\mathbf{k}'d}V_{d\mathbf{k}}}{\varepsilon_k-E_d-U}(c_{\mathbf{k}'\downarrow}{}^{+}c_{\mathbf{k}_{\downarrow}}n_{d\uparrow}+c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\uparrow}n_{d\downarrow}-c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\downarrow}S_{-}-c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\uparrow}S_{+})] \\
&= \sum_{\mathbf{k},\mathbf{k}'}[\frac{V_{\mathbf{k}'d}V_{d\mathbf{k}}}{E_d-\varepsilon_k}(-c_{\mathbf{k}\uparrow}{}^{+}c_{\mathbf{k}'\uparrow}(S_z+\frac{1}{2})-c_{\mathbf{k}\downarrow}{}^{+}c_{\mathbf{k}'\downarrow}(\frac{1}{2}-S_z)-c_{\mathbf{k}\uparrow}{}^{+}c_{\mathbf{k}'\downarrow}S_{-}-c_{\mathbf{k}\downarrow}{}^{+}c_{\mathbf{k}'\uparrow}S_{+}) \\
&\quad+\frac{V_{\mathbf{k}'d}V_{d\mathbf{k}}}{\varepsilon_k-E_d-U}(c_{\mathbf{k}'\downarrow}{}^{+}c_{\mathbf{k}_{\downarrow}}(S_z+\frac{1}{2})+c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\uparrow}(\frac{1}{2}-S_z)-c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\downarrow}S_{-}-c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\uparrow}S_{+})] \\
&= -\sum_{\mathbf{k},\mathbf{k}'}V_{\mathbf{k}'d}V_{d\mathbf{k}}[(\frac{1}{E_d-\varepsilon_k}+\frac{1}{\varepsilon_k-E_d-U})(c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\downarrow}S_{-}+c_{\mathbf{k}'\downarrow}{}^{+}c_{\mathbf{k}\uparrow}S_{+}+(c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\uparrow}-c_{\mathbf{k}'\downarrow}{}^{+}c_{\mathbf{k}_{\downarrow}})S_z \\
&\quad-\frac{1}{2}\sum_{\mathbf{k},\mathbf{k}}V_{\mathbf{k}'d}V_{d\mathbf{k}}(\frac{1}{E_d-\varepsilon_k}-\frac{1}{\varepsilon_k-E_d-U})(c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\uparrow}+c_{\mathbf{k}'\downarrow}{}^{+}c_{\mathbf{k}_{\downarrow}})
\end{aligned}$$

Since the second term of $H^{(2)}$ has nothing to do with the interactions, the second term is moved to the Hamiltonaian $H^{(1)}$. Then we have

$$\begin{aligned}
H^{(0)} &= \frac{1}{2}\sum_{\mathbf{k},\mathbf{k}'}V_{\mathbf{k}'d}V_{d\mathbf{k}}[(\frac{1}{E_d-\varepsilon_k}-\frac{1}{\varepsilon_k-E_d-U})(c_{\mathbf{k}'\downarrow}{}^{+}c_{\mathbf{k}\downarrow}+c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\uparrow}) \\
&\quad+\frac{1}{\varepsilon_k-E_d-U}\delta_{\mathbf{k},\mathbf{k}'}n_d]
\end{aligned}$$

$$\begin{aligned}
H_{ex} &= -\sum_{\mathbf{k},\mathbf{k}'}V_{\mathbf{k}'d}V_{d\mathbf{k}}[(\frac{1}{E_d-\varepsilon_k}+\frac{1}{\varepsilon_k-E_d-U})\{(c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\uparrow}-c_{\mathbf{k}'\downarrow}{}^{+}c_{\mathbf{k}_{\downarrow}})S_z \\
&\quad+c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\downarrow}S_{-}+c_{\mathbf{k}'\downarrow}{}^{+}c_{\mathbf{k}\uparrow}S_{+}\}
\end{aligned}$$

The s-d exchange interaction H_{ex} can be expressed by

$$H_{ex}=-\frac{J}{2N}\sum_{\mathbf{k},\mathbf{k}'}\{(c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\uparrow}-c_{\mathbf{k}'\downarrow}{}^{+}c_{\mathbf{k}_{\downarrow}})S_z+c_{\mathbf{k}'\uparrow}{}^{+}c_{\mathbf{k}\downarrow}S_{-}+c_{\mathbf{k}'\downarrow}{}^{+}c_{\mathbf{k}\uparrow}S_{+}\}$$

We use the approximation

$$V_{\mathbf{k}'d}=V_{d\mathbf{k}}=V$$

$$\begin{aligned}\frac{J}{2N} &= V^2\left(\frac{1}{E_d-\varepsilon_k}+\frac{1}{\varepsilon_k-E_d-U}\right)\\ &= V^2\left(\frac{1}{E_d-\varepsilon_F-\varepsilon_k+\varepsilon_F}+\frac{1}{\varepsilon_k-\varepsilon_F-E_d+\varepsilon_F-U}\right)\\ &\approx -V^2\left(\frac{1}{|\varepsilon_d|}+\frac{1}{\varepsilon_d+U}\right)\end{aligned}$$

where $\varepsilon_d = E_d-\varepsilon_F < 0$, and $\varepsilon_k \approx \varepsilon_F$ .Since $U > |\varepsilon_d| > 0$, J is negative, which is indicative of antiferromagnetic interaction.

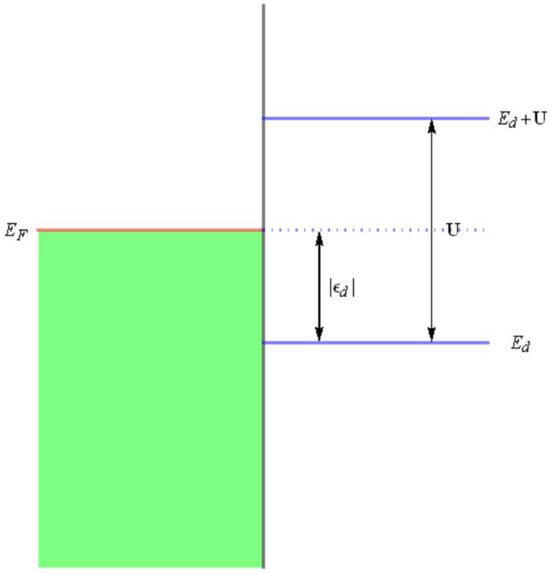


Fig. $\varepsilon_d = E_d - E_F$ (<0). Note that $|\varepsilon_d| << U$

Then we get

$$H_{ex} = -\frac{J}{2N}\sum_{\substack{\boldsymbol{k},\boldsymbol{k}'\\ \alpha,\beta}} c_{\boldsymbol{k}'\alpha}{}^{+}\boldsymbol{\sigma}_{\alpha\beta}c_{\boldsymbol{k}\beta}\cdot\boldsymbol{S}$$

Note that

$$\begin{aligned}\sum_{\alpha,\beta} c_{\boldsymbol{k}'\alpha}{}^{+}\boldsymbol{\sigma}_{\alpha\beta}c_{\boldsymbol{k}\beta}\cdot\boldsymbol{S} &= (c_{\boldsymbol{k}'1}{}^{+}\sigma^x_{11}c_{\boldsymbol{k}1} + c_{\boldsymbol{k}'1}{}^{+}\sigma^x_{12}c_{\boldsymbol{k}2} + c_{\boldsymbol{k}'2}{}^{+}\sigma^x_{21}c_{\boldsymbol{k}1} + c_{\boldsymbol{k}'2}{}^{+}\sigma^x_{22}c_{\boldsymbol{k}2})\cdot S_x \\
&\quad + (c_{\boldsymbol{k}'1}{}^{+}\sigma^y_{11}c_{\boldsymbol{k}1} + c_{\boldsymbol{k}'1}{}^{+}\sigma^y_{12}c_{\boldsymbol{k}2} + c_{\boldsymbol{k}'2}{}^{+}\sigma^y_{21}c_{\boldsymbol{k}1} + c_{\boldsymbol{k}'2}{}^{+}\sigma^y_{22}c_{\boldsymbol{k}2})\cdot S_y \\
&\quad + (c_{\boldsymbol{k}'1}{}^{+}\sigma^z_{11}c_{\boldsymbol{k}1} + c_{\boldsymbol{k}'1}{}^{+}\sigma^z_{12}c_{\boldsymbol{k}2} + c_{\boldsymbol{k}'2}{}^{+}\sigma^z_{21}c_{\boldsymbol{k}1} + c_{\boldsymbol{k}'2}{}^{+}\sigma^z_{22}c_{\boldsymbol{k}2})\cdot S_z \\
&= (c_{\boldsymbol{k}'1}{}^{+}c_{\boldsymbol{k}2} + c_{\boldsymbol{k}'2}{}^{+}c_{\boldsymbol{k}1})\cdot S_x \\
&\quad + (-ic_{\boldsymbol{k}'1}{}^{+}c_{\boldsymbol{k}2} + c_{\boldsymbol{k}'2}{}^{+}ic_{\boldsymbol{k}1})\cdot S_y \\
&\quad + (c_{\boldsymbol{k}'1}{}^{+}c_{\boldsymbol{k}1} - c_{\boldsymbol{k}'2}{}^{+}c_{\boldsymbol{k}2})\cdot S_z \\
&= c_{\boldsymbol{k}'1}{}^{+}c_{\boldsymbol{k}2}(S_x - iS_y) + c_{\boldsymbol{k}'2}{}^{+}c_{\boldsymbol{k}1}(S_x + iS_y) + (c_{\boldsymbol{k}'1}{}^{+}c_{\boldsymbol{k}1} - c_{\boldsymbol{k}'2}{}^{+}c_{\boldsymbol{k}2})\cdot S_z \\
&= c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\downarrow}S_- + c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\uparrow}S_+ + (c_{\boldsymbol{k}'\uparrow}{}^{+}c_{\boldsymbol{k}\uparrow} - c_{\boldsymbol{k}'\downarrow}{}^{+}c_{\boldsymbol{k}\downarrow})\cdot S_z\end{aligned}$$

where the Pauli matrices are given by

$$\sigma^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \qquad \sigma^y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \qquad \sigma^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

In conclusion, the Anderson Hamiltonain is equivalent to the s-d exchange interaction when the mixing term V is small and the impurity d-band is occupied by one electron. In this limit, the Anderson Hamiltonian leads to the Kondo effect and gives rise to the singlet ground state.,

8. Calculation of electrical resistivity due to the s-d interaction

The electrical conductivity is represented by the mean free time $\tau_{\mathbf{k}}$ and the Fermi velocity of electron $\boldsymbol{v}_{\mathbf{k}}$ as

$$\sigma = -\frac{2e^2}{3\Omega}\int d\varepsilon_{\boldsymbol{k}}\tau_{\boldsymbol{k}}v_{\boldsymbol{k}}\rho(\varepsilon_{\boldsymbol{k}})\frac{\partial f}{\partial\varepsilon_{\boldsymbol{k}}}$$

where Ω and $\rho(\varepsilon_{\boldsymbol{k}})$ are the volume of the system and the density of states for the conduction electrons, respectively. In general, the scattering probability $1/\tau(\varepsilon)$ is given by the *T*-matrix as

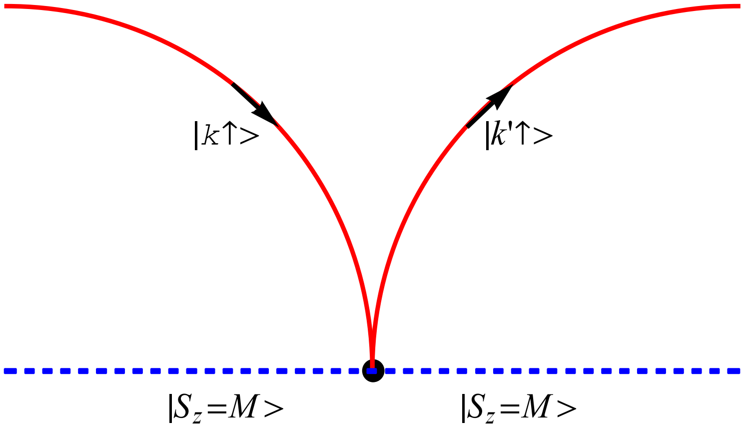
$$\frac{1}{\tau(\varepsilon)} = \frac{2\pi}{\hbar}\sum_f \left|\langle f|T(\varepsilon)|i\rangle\right|^2 \delta(\varepsilon - \varepsilon_f + \varepsilon_i),$$

where $|i\rangle$ and $|f\rangle$ are the initial and final states, respectively. The T-matrix is given by

$$T = H_{s-d} + H_{s-d}\frac{1}{E - H_0}H_{s-d}$$

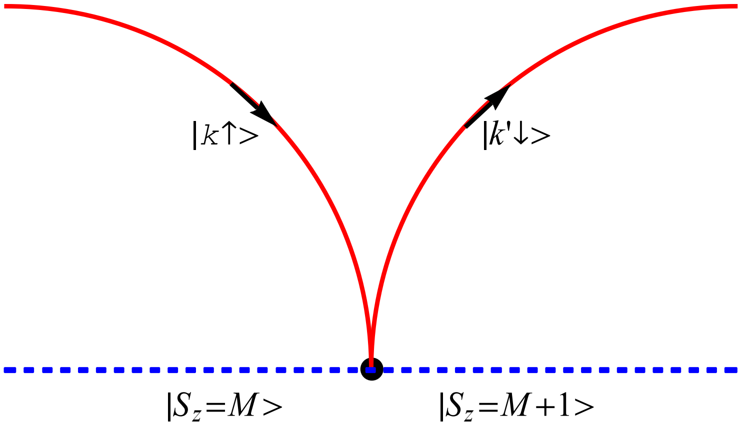
where η is an infinitesimal positive number, and H_{sd} is the scattering potential.

The first-order term of the T-matrix for the scattering of conduction electron; $\left|\boldsymbol{k},\uparrow\right\rangle \rightarrow \left|\boldsymbol{k}',\uparrow\right\rangle$



$$
\begin{aligned}
T^{(1)}(\left|\boldsymbol{k},\uparrow\right\rangle \rightarrow \left|\boldsymbol{k}',\uparrow\right\rangle) &= \left\langle f\right|H_{s-d}\left|i\right\rangle \\
&= -\frac{J}{2N}\left\langle \uparrow, M\right|\boldsymbol{\sigma}\cdot\boldsymbol{S}\left|\uparrow, M\right\rangle \\
&= -\frac{J}{2N}\left\langle M\right|S_z\left|M\right\rangle
\end{aligned}
$$

The first -order term accompanying the spin flip for the scattering; $\left|\boldsymbol{k},\uparrow\right\rangle \rightarrow \left|\boldsymbol{k}',\downarrow\right\rangle$



$$\begin{aligned} T^{(1)}(\left|\boldsymbol{k},\uparrow\right\rangle \to \left|\boldsymbol{k}',\downarrow\right\rangle) &= -\frac{J}{2N}\left\langle M+1\left|S_+\right|M\right\rangle \\ &= -\frac{J}{2N}\left\langle \downarrow, M+1\left|\boldsymbol{\sigma}\cdot\boldsymbol{S}\right|\uparrow, M\right\rangle \\ &= -\frac{J}{2N}\sqrt{(S-M)(S+M+1)} \end{aligned}$$

((Note))

(i)

$$\begin{aligned} \left\langle \sigma_z'', M''\left|\boldsymbol{\sigma}\cdot\boldsymbol{S}\right|\uparrow, M\right\rangle &= \left\langle \sigma_z'', M''\left|\sigma_z S_z + \frac{1}{2}(\sigma_+ S_- + \sigma_- S_+)\right|\uparrow, M\right\rangle \\ &= \delta(\sigma_z'', 1)\delta(M'', M)\left\langle M\left|S_z\right|M\right\rangle \\ &\quad + \delta(\sigma_z'', -1)\delta(M'', M+1)\left\langle M+1\left|S_+\right|M\right\rangle \end{aligned}$$

or

$$\left\langle \uparrow, M\left|\boldsymbol{\sigma}\cdot\boldsymbol{S}\right|\uparrow, M\right\rangle = \left\langle M\left|S_z\right|M\right\rangle$$

$$\left\langle \downarrow, M+1\left|\boldsymbol{\sigma}\cdot\boldsymbol{S}\right|\uparrow, M\right\rangle = \left\langle M+1\left|S_+\right|M\right\rangle$$

(ii)

$$\begin{aligned} \left\langle \sigma_z'', M''\left|\boldsymbol{\sigma}\cdot\boldsymbol{S}\right|\downarrow, M\right\rangle &= \left\langle \sigma_z'', M''\left|\sigma_z S_z + \frac{1}{2}(\sigma_+ S_- + \sigma_- S_+)\right|\downarrow, M\right\rangle \\ &= \left\langle \sigma_z'', M''\left|S_z + \frac{1}{2}\sigma_+ S_-\right|\downarrow, M\right\rangle \\ &= \delta(\sigma_z'', -1)\delta(M'', M)\left\langle M\left|S_z\right|M\right\rangle + \\ &\quad + \delta(\sigma_z'', 1)\delta(M'', M-1)\left\langle M-1\left|S_-\right|M\right\rangle \end{aligned}$$

$$\left\langle \downarrow, M\left|\boldsymbol{\sigma}\cdot\boldsymbol{S}\right|\downarrow, M\right\rangle = \left\langle M\left|S_z\right|M\right\rangle$$

$$\left\langle \uparrow, M-1\left|\boldsymbol{\sigma}\cdot\boldsymbol{S}\right|\downarrow, M\right\rangle = \left\langle M-1\left|S_-\right|M\right\rangle$$

$$\sigma_z\left|\uparrow\right\rangle=\left|\uparrow\right\rangle, \qquad \sigma_z\left|\downarrow\right\rangle=-\left|\downarrow\right\rangle,$$

$$\frac{1}{2}\sigma_+\left|\uparrow\right\rangle=0, \qquad \frac{1}{2}\sigma_+\left|\downarrow\right\rangle=\left|\uparrow\right\rangle$$

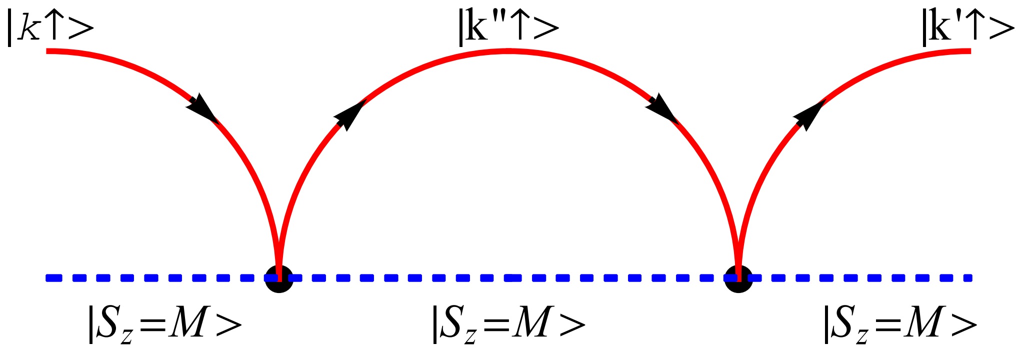
$$\frac{1}{2}\sigma_-\left|\uparrow\right\rangle=\left|\downarrow\right\rangle, \qquad \frac{1}{2}\sigma_-\left|\downarrow\right\rangle=0$$

Then the total *T*-matrix up to the first-order is given by

$$T^{(1)}=-\frac{J}{2N}(\boldsymbol{\sigma}\cdot\boldsymbol{S}).$$

We now consider the four second-order terms shown by (a) – (d).

(a) The process: $\left|\boldsymbol{k}\uparrow\right\rangle\rightarrow\left|\boldsymbol{k}''\uparrow\right\rangle\rightarrow\left|\boldsymbol{k}'\uparrow\right\rangle$ (without spin flip)



The *T*-matrix is given by

$$\left(\frac{J}{2N}\right)^2\sum_{k''}\frac{1-f_{k''}}{\varepsilon-\varepsilon_{k''}+i\eta}\left\langle M\left|S_z{}^2\right|M\right\rangle$$

(b)

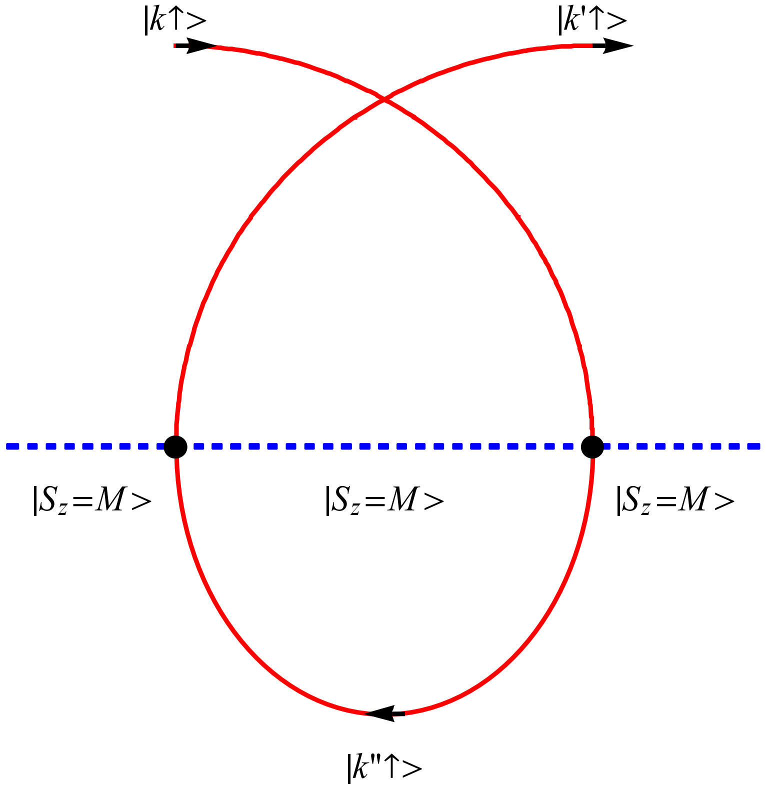


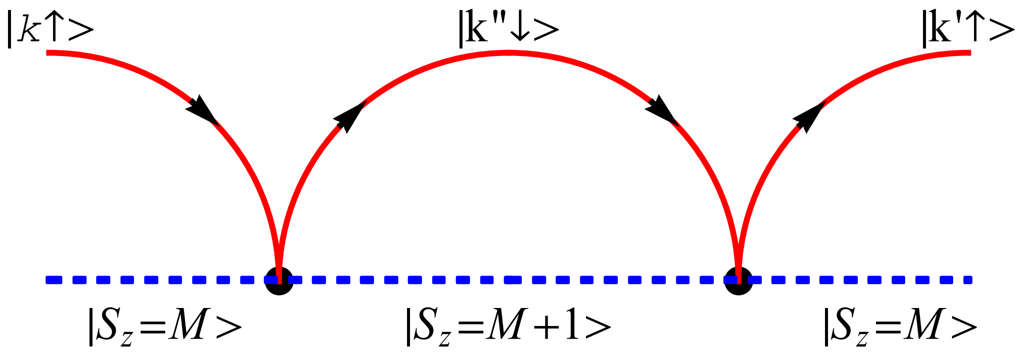
Fig. The arrow directed to the left denotes holes, while the arrow directed to the right denotes electrons.

$$(\frac{J}{2N})^2 \sum_{k"} \frac{f_{k"}}{\varepsilon - \varepsilon_{k"} + i\eta} \langle M | S_z{}^2 | M \rangle$$

where we have fixed the energy of the electrons in the initial state and final states at

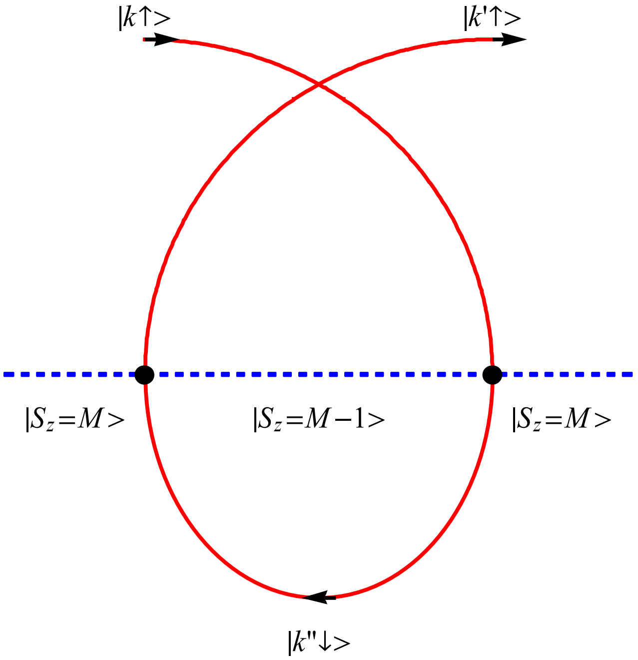
$$\varepsilon_k = \varepsilon_{k'} = \varepsilon + i\eta$$

(c)



$$(\frac{J}{2N})^2\sum_{k''}\frac{(1-f_{k''})}{\varepsilon-\varepsilon_{k''}+i\eta}\langle M|S_-S_+|M\rangle$$

(d)



$$(\frac{J}{2N})^2\sum_{k''}\frac{f_{k''}}{\varepsilon-\varepsilon_{k''}+i\eta}\langle M|S_+S_-|M\rangle]$$

Combining the four second-order processes (a) – (d), we have

$$T^{(2)}(\left|\boldsymbol{k}\uparrow\right\rangle \to \left|\boldsymbol{k}'\uparrow\right\rangle) = (\frac{J}{2N})^2 \sum_{\boldsymbol{k}''} \{ \frac{1}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} \langle M | S_z{}^2 | M \rangle + \frac{1 - f_{\boldsymbol{k}''}}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} \langle M | S_- S_+ | M \rangle$$

$$+ \frac{f_{\boldsymbol{k}''}}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} \langle M | S_+ S_- | M \rangle \}$$

$$= (\frac{J}{2N})^2 \sum_{\boldsymbol{k}''} \{ \frac{1}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} S(S+1) - \frac{1 - 2f_{\boldsymbol{k}''}}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} \langle M | S_z | M \rangle \}$$

Here we note that

$$S_\pm S_\mp = S(S+1) - S_z{}^2 \pm S_z$$

In a similar way to $\left|\boldsymbol{k}\uparrow\right\rangle \to \left|\boldsymbol{k}'\uparrow\right\rangle$, the second-order term of the *T*-matrix for the scattering for the process $\left|\boldsymbol{k}\uparrow\right\rangle \to \left|\boldsymbol{k}'\downarrow\right\rangle$ is obtained as

$$T^{(2)}(\left|\boldsymbol{k}\uparrow\right\rangle \to \left|\boldsymbol{k}'\downarrow\right\rangle) = -(\frac{J}{2N})^2 \sum_{\boldsymbol{k}''} \frac{1 - 2f_{\boldsymbol{k}''}}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} \langle M+1 | S_+ | M \rangle$$

Finally, the total *T*-matrix up to the second order terms is given by

$$T^{(2)} = (\frac{J}{2N})^2 \sum_{\boldsymbol{k}''} \{ \frac{1}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} S(S+1) - (\boldsymbol{\sigma} \cdot \boldsymbol{S}) \frac{1 - 2f_{\boldsymbol{k}''}}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} \}$$

and

$$T^{(1)+(2)} = (\frac{J}{2N})^2 \sum_{\boldsymbol{k}''} \frac{1}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} S(S+1) - \frac{J}{2N} (\boldsymbol{\sigma} \cdot \boldsymbol{S}) \{ 1 + \frac{J}{2N} \sum_{\boldsymbol{k}''} \frac{1 - 2f_{\boldsymbol{k}''}}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} \}$$

$$-\left(\frac{J}{2N}\right)^2 \sum_{\boldsymbol{k}''} \frac{1 - 2f_{\boldsymbol{k}''}}{\varepsilon - \varepsilon_{\boldsymbol{k}''} + i\eta} = -\left(\frac{J}{2N}\right)^2 \int_{-\infty}^{\infty} d\varepsilon' \rho(\varepsilon') \frac{1 - 2f(\varepsilon')}{\varepsilon - \varepsilon' + i\eta}$$

$$= -\left(\frac{J}{2N}\right)^2 \int_{-\infty}^{\infty} d\varepsilon' \rho(\varepsilon') 1 - 2f(\varepsilon') [\frac{1}{\varepsilon - \varepsilon'} - i\pi\delta(\varepsilon - \varepsilon')]$$

$$= -\left(\frac{J}{2N}\right)^2 \int_{-\infty}^{\infty} d\varepsilon' \rho(\varepsilon') \frac{1 - 2f(\varepsilon')}{\varepsilon - \varepsilon'} + i\pi \left(\frac{J}{2N}\right)^2 \int_{-\infty}^{\infty} d\varepsilon' \rho(\varepsilon') [1 - 2f(\varepsilon')] \delta(\varepsilon - \varepsilon')$$

$$= -\left(\frac{J}{2N}\right)^2 \int_{-\infty}^{\infty} d\varepsilon' \rho(\varepsilon') \frac{1 - 2f(\varepsilon')}{\varepsilon - \varepsilon'} + i\pi \left(\frac{J}{2N}\right)^2 \rho(\varepsilon) [1 - 2f(\varepsilon)]$$

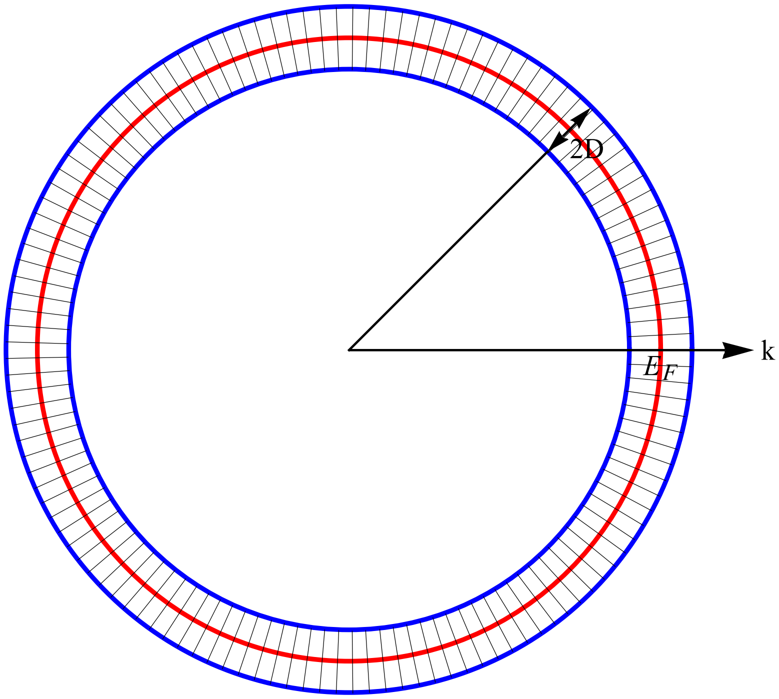


Fig. The region in momentum space relevant to the formulation of the Kondo effect. At low temperatures where we are interested, we may linearize the spectrum around ε_F and impose a cut off D.

We assume the following density of states for the conduction electrons,

$$\rho(\varepsilon)=\rho \qquad \text{for } |\varepsilon-\varepsilon_F|<D\,, \qquad \rho(\varepsilon)=0 \qquad \text{for } |\varepsilon-\varepsilon_F|>D\,,$$

The first term:

$$-\left(\frac{J}{2N}\right)^2\int_0^\infty d\varepsilon'\,\rho(\varepsilon')\frac{1-2f(\varepsilon')}{\varepsilon-\varepsilon'}=\left(\frac{J}{2N}\right)^2\rho\int_{-D+\varepsilon_F}^{D+\varepsilon_F} d\varepsilon'\frac{1-2f(\varepsilon')}{\varepsilon'-\varepsilon}$$

We now calculate the integral,

$$I = \int_{-D+\varepsilon_F}^{D+\varepsilon_F} d\varepsilon' \frac{1-2f(\varepsilon')}{\varepsilon'-\varepsilon}$$

$$= \ln\left|D+\varepsilon_F-\varepsilon\right| + \ln\left|D-\varepsilon_F+\varepsilon\right| - 2\int_{-D+\varepsilon_F}^{D+\varepsilon_F} \ln\left|\varepsilon-\varepsilon'\right|\left(-\frac{\partial f(\varepsilon')}{\partial\varepsilon'}\right)d\varepsilon'$$

$$= \ln\left|D-\varepsilon_r\right| + \ln\left|D+\varepsilon_r\right| + I^{(2)}$$

$$\approx 2\ln D + I^{(2)}$$

where

$$\varepsilon_r = \varepsilon - \varepsilon_F .$$

Since

$$f(\varepsilon') = \frac{1}{e^{\beta(\varepsilon'-\varepsilon_F)}+1},$$

$$\frac{\partial}{\partial\varepsilon'}f(\varepsilon') = -\frac{\beta e^{\beta(\varepsilon'-\varepsilon_F)}}{[e^{\beta(\varepsilon'-\varepsilon_F)}+1]^2} = -\beta \sec h^2[\frac{\beta(\varepsilon'-\varepsilon_F)}{2}]$$

we get

$$\int_{-D+\varepsilon_F}^{D+\varepsilon_F} \ln\left|\varepsilon-\varepsilon'\right|\left(-\frac{\partial f(\varepsilon')}{\partial\varepsilon'}\right)d\varepsilon' = \beta\int_{-D+\varepsilon_F}^{D+\varepsilon_F} \ln\left|\varepsilon-\varepsilon'\right| \sec h^2[\frac{\beta(\varepsilon'-\varepsilon_F)}{2}]d\varepsilon'$$

Here we put

$$\varepsilon'-\varepsilon_F = x,$$

Then the second term of *I* is

$$I^{(2)} = -2\beta\int_{-D}^{D} \ln\left|\varepsilon_r - x\right| \sec h^2(\frac{\beta x}{2})dx \approx -2\beta\int_{-\infty}^{\infty} \ln\left|\varepsilon_r - x\right| \sec h^2(\frac{\beta x}{2})dx$$

(i) $\left|\varepsilon_r\right| >> k_B T$

$$I^{(2)} \approx -2\beta \ln|\varepsilon_r| \int_{-\infty}^{\infty} \sec h^2(\frac{\beta x}{2})dx = -8\ln|\varepsilon_r|$$

and

$$I = 2\ln D - 8\ln|\varepsilon| = -6\ln D - 8\ln\frac{|\varepsilon|}{D}$$

(ii) $|\varepsilon_r| << k_B T$

$$\begin{aligned}
I^{(2)} &\approx -2\beta \int_{-\infty}^{\infty} \ln|x| \sec h^2(\frac{\beta x}{2})dx \\
&= -4\int_{-\infty}^{\infty} dy[\ln(\frac{2}{\beta}) + \ln|y|]\sec h^2(y) \\
&= -4\ln(\frac{2}{\beta})\int_{-\infty}^{\infty} dy \sec h^2(y) - 4\int_{-\infty}^{\infty} dy \ln|y|]\sec h^2(y) \\
&= -8\ln(\frac{2}{\beta}) - 8\int_{0}^{\infty} dy \ln y \sec h^2(y)] \\
&= -8\ln(2k_B T) + 8\ln(\frac{4e^\gamma}{\pi}) = -8\ln(\frac{\pi k_B T}{2e^\gamma D})
\end{aligned}$$

$$I = -6\ln D - 8\ln(\frac{\pi k_B T}{2e^\gamma D})$$

((Note-1))

$$\int_0^{\infty} dy \ln y \sec h^2(y) = \ln(\frac{\pi}{4}) - \gamma = -\ln(\frac{4e^\gamma}{\pi}) = -0.81878$$

with

$$\gamma = 0.577216$$

((**Note-2**))

$$\int_{-\infty}^{\infty} \sec h^2(x)dx = 2$$

Thus, the T-matrix is given by

$$T^{(1)+(2)} = -\frac{J}{2N}(\boldsymbol{\sigma}\cdot\boldsymbol{S})\{1+\frac{J\rho}{N}\ln\frac{Max[|\varepsilon|,k_BT]}{D}\}$$

Thus we have the expression for the resistivity as

$$\tilde{\rho} = \tilde{\rho}_B(1+\frac{2J\rho}{N}\ln\frac{k_BT}{D}).$$

where $\tilde{\rho}_B$ is the resistivity coming from the first-order Born approximation.

9. Spin singlet for the ground state

We assume that the trial wave function is given by

$$|\psi_a\rangle = \sum_{|\boldsymbol{k}|>k_F} a_{\boldsymbol{k}}(\alpha^+ c_{\boldsymbol{k}\downarrow}{}^+ - \beta^+ c_{\boldsymbol{k}\uparrow}{}^+)|F\rangle$$

where α^+ and α^+ create up- and down-spin states of the local spin, $|F\rangle$ is the filled Fermi sea ground state, and the $a_{\mathbf{k}}$ are coefficients that we will have to determine. So this state is a spin singlet. It is antisymmetric combination of the local up-spin plus a delocalized down-spin above the Fermi surface

The Hamiltonian:

$$H_1 = -\bar{J}\sum_{\boldsymbol{k},\boldsymbol{k}'}\{(c_{\boldsymbol{k}'\uparrow}{}^+ c_{\boldsymbol{k}\uparrow} - c_{\boldsymbol{k}'\downarrow}{}^+ c_{\boldsymbol{k}_\downarrow})S_z + c_{\boldsymbol{k}'\uparrow}{}^+ c_{\boldsymbol{k}\downarrow}S_- + c_{\boldsymbol{k}'\downarrow}{}^+ c_{\boldsymbol{k}\uparrow}S_+\}$$

where

$$\bar{J} = \frac{J}{2N}.$$

The eigenvalue equation we wish to solve is

$$(H_0 + H_1 - \varepsilon_0 - \delta\varepsilon_a)|\psi_a\rangle = 0.$$

Here ε_0 is the ground-state energy of the unperturbed Hamiltonian,

$$H_0 = \sum_{\boldsymbol{k},\sigma} \varepsilon_k c_{\boldsymbol{k},\sigma}{}^{+} c_{\boldsymbol{k},\sigma}$$

and $\delta\varepsilon_a$ is the shift in energy due to the perturbation H_1. We need to determine $a_{\mathbf{k}}$ such that this shift is as negative as possible. According to Taylor, we have

$$\begin{aligned}(H_0 - \varepsilon_0 - \delta\varepsilon_a)\left|\psi_a\right\rangle &= (H_0 - \varepsilon_0 - \delta\varepsilon_a) \sum_{|\boldsymbol{k}|>k_F} a_{\boldsymbol{k}} (\alpha^{+} c_{\boldsymbol{k}\downarrow}{}^{+} - \beta^{+} c_{\boldsymbol{k}\uparrow}{}^{+})\left|F\right\rangle \\ &= \sum_{|\boldsymbol{k}|>k_F} a_{\boldsymbol{k}} (\varepsilon_k - \delta\varepsilon_a)(\alpha^{+} c_{\boldsymbol{k}\downarrow}{}^{+} - \beta^{+} c_{\boldsymbol{k}\uparrow}{}^{+})\left|F\right\rangle\end{aligned}$$

and

$$H_1\left|\psi_a\right\rangle = \frac{3\bar{J}}{2} \sum_{|\boldsymbol{k}|>k_F} a_{\boldsymbol{k}} \left|\psi_a\right\rangle = \frac{3\bar{J}}{2} \sum_{|\boldsymbol{k}|>k_F} a_{\boldsymbol{k}} \sum_{|\boldsymbol{k}'|>k_F} a_{\boldsymbol{k}'} (\alpha^{+} c_{\boldsymbol{k}'\downarrow}{}^{+} - \beta^{+} c_{\boldsymbol{k}'\uparrow}{}^{+})\left|F\right\rangle$$

The eigenvalue equation for $\delta\varepsilon_a$ then becomes

$$a_{\boldsymbol{k}} (\varepsilon_{\boldsymbol{k}} - \delta\varepsilon_a) + \frac{3\bar{J}}{2} \sum_{|\boldsymbol{k}'|>k_F} a_{\boldsymbol{k}'} = 0$$

Suppose that

$$\lambda = \sum_{|\boldsymbol{k}|>k_F} a_{\boldsymbol{k}} \ .$$

Then we get

$$a_{\boldsymbol{k}} = -\frac{3\bar{J}}{2} \frac{\lambda}{\varepsilon_{\boldsymbol{k}} - \delta\varepsilon_a} \ .$$

Then we have

$$V = \frac{2}{3\bar{J}} = \sum_{|\boldsymbol{k}|>k_F} \frac{1}{\delta\varepsilon_a - \varepsilon_{\boldsymbol{k}}},$$

where $V<0$.

((Note)) **Numerical calculation**

First we consider the simple example. Suppose that

$$N_1 = 10, \qquad 2\varepsilon_k = (2+\frac{k}{N_1})$$

where $k = 1, 2, ..., 10$. In other words,

$$2\varepsilon_k = 2, 2.1, 2.2, 2.3, \ldots, 2.8, 2.9, 3.$$

When $\delta\varepsilon_a = E$, we get

$$-\frac{1}{V} = f(E) = \sum_{k=1}^{N_1}\frac{1}{E-2\varepsilon_k} = \sum_{k=1}^{N_1}\frac{1}{E-(2+\frac{k}{N_1})} = \frac{1}{E-2.1}+\frac{1}{E-2.2}+...+\frac{1}{E-2.9}+\frac{1}{E-3}$$

We make a plot of *f*(*E*) as a function of *E*.

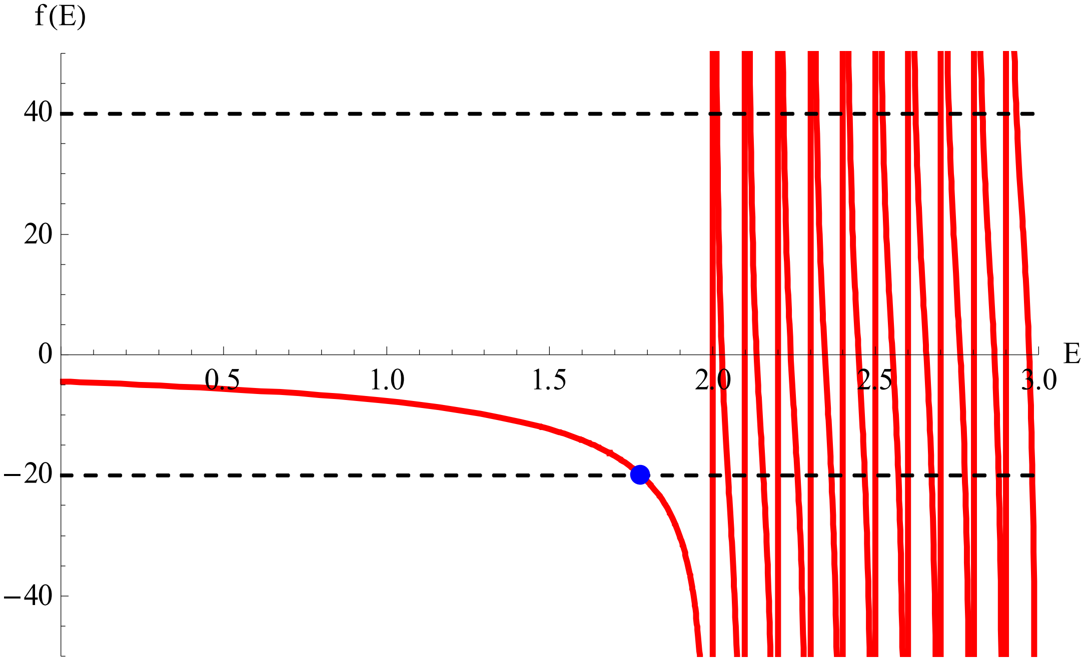
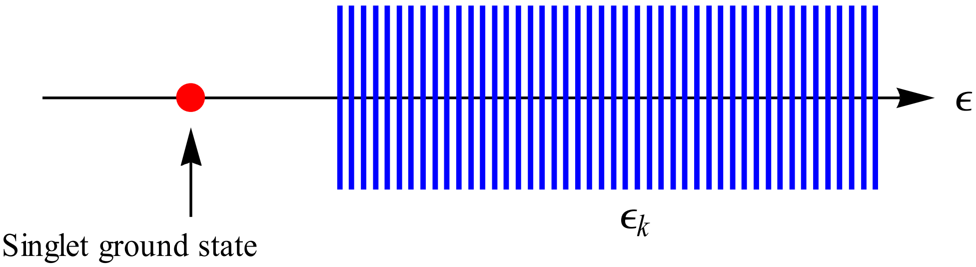


Fig. Plot of *f*(*E*) as a function of *E*. The dashed line ($-1/V = 40$) for the repulsive interaction. The dashed line ($-1/V = -20$) for the attractive interaction. The last crossing on the left is the coherent state, split from the continuum by an energy gap, displaying the essential singularity in the coupling constant.



We change from a sum over ***k*** to an integration in which the energy e measured relative to the Fermi energy run from zero to a value *D* related to the bandwidth, and approximate the density of states by its value $\rho(0)$.

$$1 = -\frac{3\bar{J}\rho}{2}\int_0^D \frac{d\varepsilon_r}{\varepsilon_r - \delta\varepsilon_a} = \frac{3\bar{J}\rho}{2}\ln\left|\frac{\delta\varepsilon_a}{D-\delta\varepsilon_a}\right|.$$

Noting that *J*<0, we then find the solution with $\delta\varepsilon_a < 0$ to be

$$\delta\varepsilon_a = -\frac{D}{\exp[\frac{2}{3|\bar{J}|}]-1}$$

This expression is reminds us of the condensation energy of a BCS superconductor. When $|\bar{J}|\rho(0)$ is small, $\delta\varepsilon_a$ is similarly given as

$$\delta\varepsilon_a = -D\exp(-\frac{2}{3|\bar{J}|\rho}) = -D\exp(-\frac{4N}{3\rho J}).$$

The state $|\psi_a\rangle$ which consists of bound spin-singlet pairs of conduction electrons and local spins, has a lower energy than ε_0, and is a better candidate for the ground state. We note that the definition of the Kondo temperature T_K is

$$k_B T_K = D\exp(-\frac{1}{2\rho\bar{J}}) = D\exp(-\frac{N}{\rho J})$$

Note that $\delta\varepsilon_a$ is related to the Kondo temperature as

$$\delta\varepsilon_a \approx -k_B T_K$$

The susceptibility at $T = 0$ K is given as

$$\chi = \frac{g^2 \mu_B{}^2}{4k_B T_K}$$

We notice an analogy with the BCS theory of superconductivity, in which we find a similar expression for the critical temperature T_c. This is not an accident. Both TK and Tc define temperatures below which perturbation theory fails. In the BCS case, Tc signals the onset of the formation of bound Cooper pairs and a new ground state with an energy gap. The Kondo effect is a little more subtle. T_K defines a temperature at which the energy contributions from the second-order perturbation theory becomes important. This happens when the local spin on a single impurity starts to become frozen out at an energy set by the Kondo coupling J and the density of states at the Fermi energy.

10. Phenomelogical interpretation

We assume that the RKKY is negligibly small. The only remaining interaction is between the impurity spin $\boldsymbol{S}$ and the conduction electron spin $\boldsymbol{s}$. It may be treated by the so-called s-d exchange interaction,

$$H = -J\boldsymbol{S}\cdot\boldsymbol{s}$$

where J (<0) is the antiferromagnetic exchange interaction.
At high tempereatures, the magnetic impurity behave like free (paramagnetic moment). Below a Kondo temperature T_K,

$$T_K \approx D\exp(-\frac{1}{\rho|J|}).$$

the isolated magnetic impurity becomes non-magnetic because of the interaction, where D is the energy band in the vicinity of the Fermi level and $N(\varepsilon_F)$ is the density of states at the Fermi level.

For $T<T_K$, there is a gradual loss of local moment as the conduction electrons begin to form a surrounding cloud of oppositely (antiferromagnetically) polarized spin. This formation is not a phase transition.

Experimental manifestations of the Kondo effect for $T<T_K$ are as follows.

(1) A loss of magnetic moment, the magnetization falls below its free moment value and the susceptibility is less than its Curie value

$$\chi_K = \frac{N\mu^2}{3k_B(T+T_K)} < \chi_C = \frac{N\mu^2}{3k_B T}$$

where

$$\mu = g\mu_B\sqrt{S(S+1)}$$

(b) The enhanced scattering rate creates a logarithmic upturn in the resistivity at low temperatures.

11. Physical properties of typical Kondo systems

It is now know that many of the properties associated with the Kondo effect can be well described by a scaling function of T/T_K.

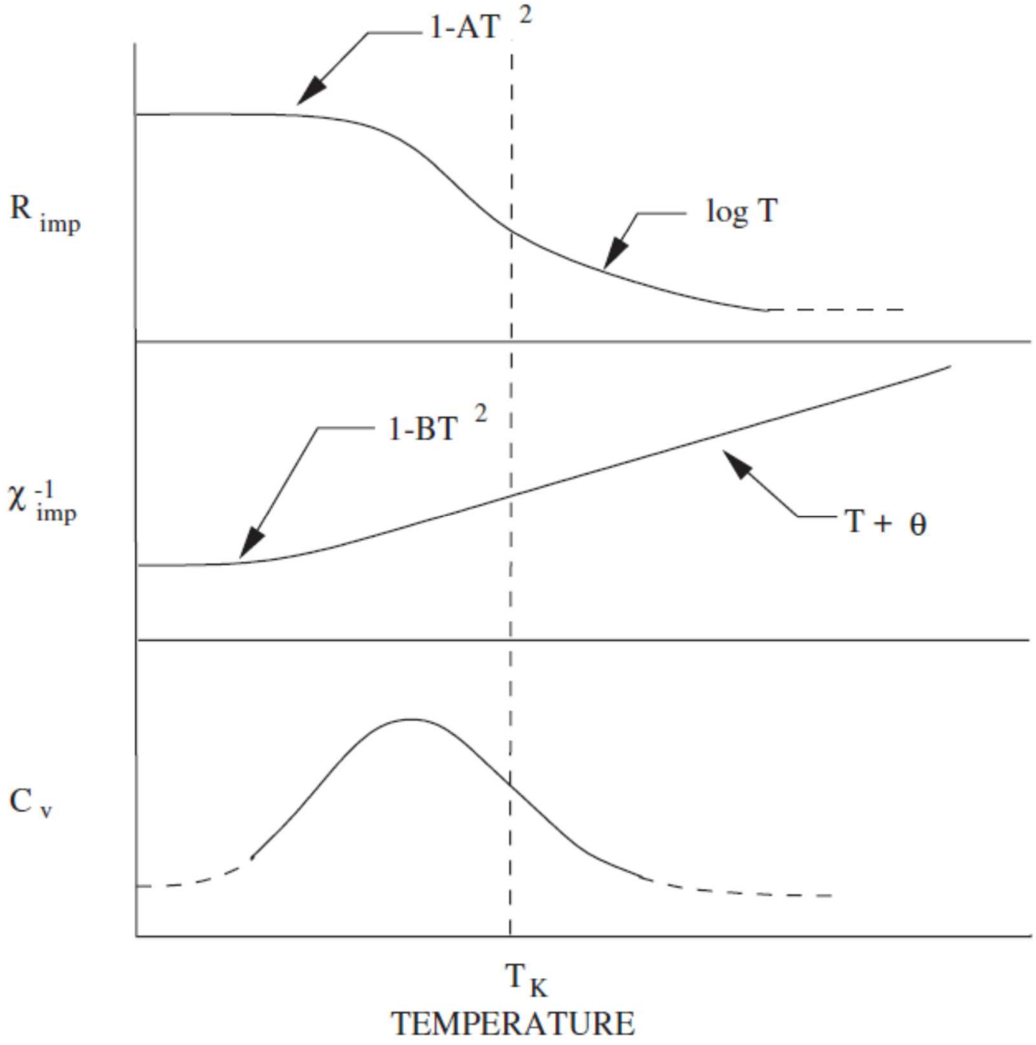


Fig. Schematic behavior characteristic of a typical Kondo alloy

(a) Resistivity

The resistivity decreases as 1-AT^2 with increasing T and varies with ln$T$ above T_K. The resistivity at 0 K is called the unitary limit.

(b) Reciprocal Susceptibility

The reciprocal susceptibility shows the Pauli paramagnetic behavior around $T = 0$ K as 1+BT^2. Above T_K, it shifts to the Curie-Weiss like behavior.

(c) Specific heat

The specific heat shows a peak below T_K, and is proportional as T^{-2} above T_K.

(d) The Wilson ratio

The specific heat is proportional to T, while the susceptibility becomes constant at $T = 0$. The Wilson ratio. The Wilson ratio is given by

$$\frac{T\chi_{imp}}{C_{imp}} = \frac{g^2 {\mu_B}^2}{{k_B}^2} 0.1521 .$$

12. Conclusion

When magnetic impurities such as Mn, Fe and Co are dilutely inserted into nonmagnetic metals such as Cu, Ag and Au, susceptibility obeying the Curie–Weiss law is observed. In this case impurity atoms are considered to possess magnetic moments. On the other hand, Mn in Al does not show the Curie–Weiss law and seems not to possess any magnetic moment. Anderson tried to explain these phenomena using the Anderson model. From the above discussions, these phenomena can be interpreted from the concept of the scaling relation. The Kondo temperature T_K is very low for Mn in Cu ($T_K \approx 0.1$ K), and is very high for Mn in Al (T_K is above room temperature).

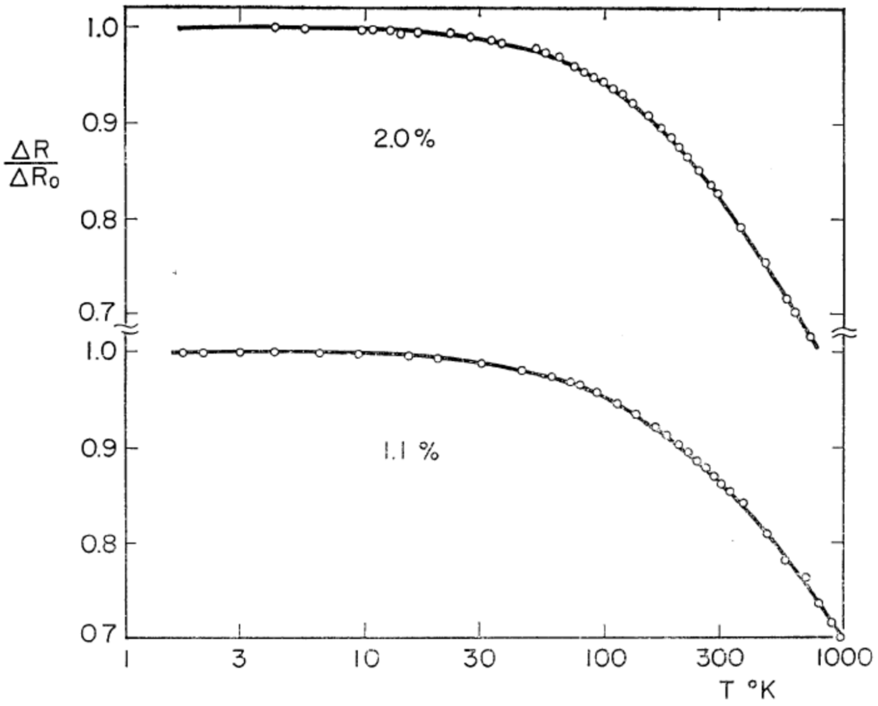


Fig. The resistivity for V (1-2 %) in Au as a function of temperature. [K. Kume (J. Phys. Soc. Jpn. 23, 1226 (1967))]. $T_K \approx 300K$ for this system. This is obtained subtracting the resistivity of pure Au from the observed resistivity.

REFERENCES

K. Yamada, *Electron correlation in metals* (Cambridge University Press, 1993, Cambridge).
J. Kondo, Solid State Pbhysics 23, 183 (1968) *Academic Press, New York).
J.Kondo, Prog. Theor. Phys. **32**, 37 (1964).
D.K.C. MacDonald, Thermoelectricity (Dover, 2006).
K. Yosida, *Theory of Magnetism* (Springer-Verlag, 1996)
J. Kondo, *The physics of dilute magnetic alloys* (Cambridge University Press, 2012).
A.C. Hewson, *The Kondo Problem toHeavy Fermions* (Cambridge, 1993).
K.H. Fisher and J.A. Hertz, *Spin Glasses* (Cambridge, 1991).
P.L. Taylor and O. Heinonen, *A Quantum Approach to Condensed Matter Physics* (Cambridge, 2002).
G. D. Mahan, *Many-Particle Physics*, 2-nd edition (Plenum Press, 1993).
K. Kume J. Phys. Soc. Jpn. **23,** 1226 (1967).
K. Yosida, *What is the Kondo effect?* (in Japanese) (Maruzen, 1990).

APPENDIX

A. Brillouin-Wigner series

(see J.M. Ziman, Element of Advanced Quantum Mechanics)

A.1

We start with the Schrodinger equation given by

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$$

with

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

Then we get

$$(\hat{H}_0 + \hat{H}_1)|\psi_n\rangle = E_n|\psi_n\rangle$$

or

$$(\hat{H}_0 + \hat{H}_1)(|\psi_n{}^{(0)}\rangle + |\Phi\rangle) = E_n(|\psi_n{}^{(0)}\rangle + |\Phi\rangle)$$

or

$$E_n|\psi_n{}^{(0)}\rangle + E_n|\Phi\rangle = (\hat{H}_0 + \hat{H}_1)|\psi_n{}^{(0)}\rangle + (\hat{H}_0 + \hat{H}_1)|\Phi\rangle)$$

or

$$E_n\left|\psi_n{}^{(0)}\right\rangle + E_n\left|\Phi\right\rangle = E_n{}^{(0)}\left|\psi_n{}^{(0)}\right\rangle + \hat{H}_0\left|\Phi\right\rangle + \hat{H}_1\left|\psi_n\right\rangle .$$

Finally we have

$$(E_n - \hat{H}_0)\left|\Phi\right\rangle = \hat{H}_1\left|\psi_n\right\rangle - (E_n - E_n{}^{(0)})\left|\psi_n{}^{(0)}\right\rangle$$

Projecting on both sides with $\hat{P}$

$$\hat{P}(E_n - \hat{H}_0)\left|\Phi\right\rangle = \hat{P}\hat{H}_1\left|\psi_n\right\rangle - (E_n - E_n{}^{(0)})\hat{P}\left|\psi_n{}^{(0)}\right\rangle$$

or

$$(E_n - \hat{H}_0)\hat{P}\left|\Phi\right\rangle = \hat{P}\hat{H}_1\left|\psi_n\right\rangle$$

or

$$(E_n - \hat{H}_0)\left|\Phi\right\rangle = \hat{P}\hat{H}_1\left|\psi_n\right\rangle$$

or

$$\left|\Phi\right\rangle = (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1\left|\psi_n\right\rangle$$

Here we use the commutation relation

$$[\hat{H}_0, \hat{P}] = 0 .$$

Thus we get the final form

$$\left|\psi_n\right\rangle = \left|\psi_n{}^{(0)}\right\rangle + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1\left|\psi_n\right\rangle$$

We solve this by iteration

$$
\begin{aligned}
|\psi_n\rangle &= |\psi_n{}^{(0)}\rangle + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(|\psi_n{}^{(0)}\rangle + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n\rangle) \\
&= |\psi_n{}^{(0)}\rangle + (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n{}^{(0)}\rangle \\
&+ (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n{}^{(0)}\rangle + \\
&+ (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n{}^{(0)}\rangle + \\
&+ (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1|\psi_n{}^{(0)}\rangle + \ldots
\end{aligned}
$$

A.2. Energy shift

What is the energy shift due to the perturbation? To this end, we start with

$$(E_n - \hat{H}_0)|\psi_n\rangle = \hat{H}_1|\psi_n\rangle$$

Projecting on both sides with $\hat{M}$

$$\hat{M}(E_n - \hat{H}_0)|\psi_n\rangle = \hat{M}\hat{H}_1|\psi_n\rangle$$

or

$$(E_n - \hat{H}_0)\hat{M}|\psi_n\rangle = \hat{M}\hat{H}_1|\psi_n\rangle$$

or

$$(E_n - \hat{H}_0)|\psi_n{}^{(0)}\rangle = \hat{M}\hat{H}_1|\psi_n\rangle,$$

where we use the commutation relation,

$$[\hat{M}, \hat{H}_0] = 0.$$

Multiplying on both sides with $\langle\psi_n{}^{(0)}|$

$$\langle\psi_n{}^{(0)}|(E_n - \hat{H}_0)|\psi_n{}^{(0)}\rangle = \langle\psi_n{}^{(0)}|\hat{M}\hat{H}_1|\psi_n{}^{(0)}\rangle$$

Then the energy shift is obtained as

$$E_n - E_n^{(0)} = \langle \psi_n^{(0)} | \hat{M}\hat{H}_1 | \psi_n^{(0)} \rangle = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle$$

Through the iteration, we have

$$\begin{aligned} E_n - E_n^{(0)} &= \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle + \langle \psi_n^{(0)} | \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 | \psi_n^{(0)} \rangle \\ &\quad + \langle \psi_n^{(0)} | \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 | \psi_n^{(0)} \rangle + \\ &\quad + \langle \psi_n^{(0)} | \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 | \psi_n^{(0)} \rangle + \end{aligned}$$

(i) The first-order energy shift:

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle .$$

The second-order energy shift:

$$\begin{aligned} E_n^{(2)} &= \langle \psi_n^{(0)} | \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P}\hat{H}_1 | \psi_n^{(0)} \rangle \\ &= \sum_{k \neq n} \langle \psi_n^{(0)} | \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P} | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle \\ &= \sum_{k \neq n} \frac{\left| \langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \right|^2}{E_n - E_k^{(0)}} \end{aligned}$$

When $E_n \to E_n^{(0)}$, we get a “Rayleigh-Schrödinger series of conventional perturbation theory.”

(ii) The second order of the energy shift:

$$E_n^{(2)} = \sum_{k \neq n} \frac{\langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}}$$

where $E_n \to E_n^{(0)}$.

(iii)` The third order of the energy shift:

$$E_n^{(3)} = \langle \psi_n^{(0)} | \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P} \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P} \hat{H}_1 | \psi_n^{(0)} \rangle$$

$$= \sum_{k\neq n. l\neq n} \langle \psi_n^{(0)} | \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P} | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 (E_n - \hat{H}_0)^{-1} \hat{P} | \psi_l^{(0)} \rangle \langle \psi_l^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle$$

$$= \sum_{k\neq n. l\neq n} \frac{\langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_l^{(0)} \rangle \langle \psi_l^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n - E_k^{(0)})(E_n - E_l^{(0)})}$$

or

$$E_n^{(3)} \approx \sum_{k\neq n. l\neq n} \frac{\langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_l^{(0)} \rangle \langle \psi_l^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})}$$

where $E_n \to E_n^{(0)}$.

(iv) The fourth-order of the energy shift

$$E_n^{(4)} \approx \sum_{\substack{k\neq n. l\neq n \\ m\neq n}} \frac{\langle \psi_n^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_l^{(0)} \rangle \langle \psi_l^{(0)} | \hat{H}_1 | \psi_m^{(0)} \rangle \langle \psi_m^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})(E_n^{(0)} - E_m^{(0)})}$$

where $E_n \to E_n^{(0)}$.

A.3 The form of $|\Phi\rangle$

Next we discuss the from of $|\Phi\rangle$.

(i) The first order of wave function:

$$|\psi_n^{(1)}\rangle = (E_n - \hat{H}_0)^{-1} \hat{P} \hat{H}_1 | \psi_n^{(0)} \rangle$$

$$= \sum_{k\neq n} (E_n - \hat{H}_0)^{-1} \hat{P} | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle$$

$$= \sum_{k\neq n} \frac{| \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n - E_k^{(0)})}$$

or

$$|\psi_n^{(1)}\rangle \approx \sum_{k\neq n} \frac{| \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{(E_n^{(0)} - E_k^{(0)})}$$

where $E_n \to E_n{}^{(0)}$.

(ii) The second order of the wave function:

$$\begin{aligned}\left|\psi_n{}^{(2)}\right\rangle &= (E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\hat{H}_1\left|\psi_n{}^{(0)}\right\rangle \\ &= \sum_{k\neq n, l\neq n}(E_n - \hat{H}_0)^{-1}\hat{P}\left|\psi_k{}^{(0)}\right\rangle\left\langle\psi_k{}^{(0)}\right|\hat{H}_1(E_n - \hat{H}_0)^{-1}\hat{P}\left|\psi_l{}^{(0)}\right\rangle\left\langle\psi_l{}^{(0)}\right|\hat{H}_1\left|\psi_n{}^{(0)}\right\langle \\ &= \sum_{k\neq n, l\neq n}\frac{\left|\psi_k{}^{(0)}\right\rangle\left\langle\psi_k{}^{(0)}\right|\hat{H}_1\left|\psi_l{}^{(0)}\right\rangle\left\langle\psi_l{}^{(0)}\right|\hat{H}_1\left|\psi_n{}^{(0)}\right\rangle}{(E_n{}^{(0)} - E_k{}^{(0)})(E_n{}^{(0)} - E_l{}^{(0)})}\end{aligned}$$

or

$$\left|\psi_n{}^{(2)}\right\rangle = \sum_{k\neq n, l\neq n}\frac{\left|\psi_k{}^{(0)}\right\rangle\left\langle\psi_k{}^{(0)}\right|\hat{H}_1\left|\psi_l{}^{(0)}\right\rangle\left\langle\psi_l{}^{(0)}\right|\hat{H}_1\left|\psi_n{}^{(0)}\right\rangle}{(E_n{}^{(0)} - E_k{}^{(0)})(E_n{}^{(0)} - E_l{}^{(0)})}$$

where $E_n \to E_n{}^{(0)}$.

(iii) The third order of the wave function:

$$\left|\psi_n{}^{(3)}\right\rangle \approx \sum_{\substack{k\neq n, l\neq n\\ m\neq n}}\frac{\left|\psi_k{}^{(0)}\right\rangle\left\langle\psi_k{}^{(0)}\right|\hat{H}_1\left|\psi_l{}^{(0)}\right\rangle\left\langle\psi_l{}^{(0)}\right|\hat{H}_1\left|\psi_m{}^{(0)}\right\rangle\left\langle\psi_m{}^{(0)}\right|\hat{H}_1\left|\psi_n{}^{(0)}\right\rangle}{(E_n{}^{(0)} - E_k{}^{(0)})(E_n{}^{(0)} - E_l{}^{(0)})(E_n{}^{(0)} - E_m{}^{(0)})}.$$

(iv) The fourth order of the wave function:

$$\left|\psi_n{}^{(4)}\right\rangle \approx \sum_{\substack{k\neq n, l\neq n\\ m\neq n}}\frac{\left|\psi_k{}^{(0)}\right\rangle\left\langle\psi_k{}^{(0)}\right|\hat{H}_1\left|\psi_l{}^{(0)}\right\rangle\left\langle\psi_l{}^{(0)}\right|\hat{H}_1\left|\psi_m{}^{(0)}\right\rangle\left\langle\psi_m{}^{(0)}\right|\hat{H}_1\left|\psi_p{}^{(0)}\right\rangle\left\langle\psi_p{}^{(0)}\right|\hat{H}_1\left|\psi_n{}^{(0)}\right\rangle}{(E_n{}^{(0)} - E_k{}^{(0)})(E_n{}^{(0)} - E_l{}^{(0)})(E_n{}^{(0)} - E_m{}^{(0)})(E_n{}^{(0)} - E_p{}^{(0)})}.$$

7 Lipmann-Schwinger equation

The Hamiltonian H is given by

$$\hat{H} = \hat{H}_0 + \hat{V}$$

where H_0 is the Hamiltonian of free particle. Let $|\phi\rangle$ be the eigenket of $H_0$with the energy eigenvalue E,

$$\hat{H}_0|\phi\rangle = E|\phi\rangle$$

The basic Schrödinger equation is

$$(\hat{H}_0 + \hat{V})|\psi\rangle = E|\psi\rangle \qquad (1)$$

Both $\hat{H}_0$ and $\hat{H}_0 + \hat{V}$ exhibit continuous energy spectra. We look for a solution to Eq.(1) such that as $V \to 0$, $|\psi\rangle \to |\phi\rangle$, where $|\phi\rangle$ is the solution to the free particle Schrödinger equation with the same energy eigenvalue E.

$$\hat{V}|\psi\rangle = (E - \hat{H}_0)|\psi\rangle$$

Since $(E - \hat{H}_0)|\phi\rangle = 0$, this can be rewritten as

$$\hat{V}|\psi\rangle = (E - \hat{H}_0)|\psi\rangle - (E - \hat{H}_0)|\phi\rangle$$

which leads to

$$(E - \hat{H}_0)(|\psi\rangle - |\phi\rangle) = \hat{V}|\psi\rangle$$

or

$$|\psi\rangle = (E - \hat{H}_0)^{-1}\hat{V}|\psi\rangle + |\phi\rangle .$$

The presence of $|\phi\rangle$ is reasonable because $|\psi\rangle$ must reduce to $|\phi\rangle$ as $\hat{V}$ vanishes.

B.1 Lipmann-Schwinger equation:

$$|\psi^{(\pm)}\rangle = |\mathbf{k}\rangle + (E_k - \hat{H}_0 \pm i\varepsilon)^{-1}\hat{V}|\psi^{(\pm)}\rangle$$

by making E_k (= $\hbar^2\mathbf{k}^2/2m$) slightly complex number (ε>0, ε≈0). This can be rewritten as

$$\langle \mathbf{r} | \psi^{(\pm)} \rangle = \langle \mathbf{r} | \mathbf{k} \rangle + \int dr' \langle \mathbf{r} | (E_k - \hat{H}_0 \pm i\varepsilon)^{-1} | \mathbf{r}' \rangle \langle \mathbf{r}' | \hat{V} | \psi^{(\pm)} \rangle$$

where

$$\langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}},$$

and

$$\hat{H}_0 | \mathbf{k}' \rangle = E_{k'} | \mathbf{k}' \rangle,$$

with

$$E_{k'} = \frac{\hbar^2}{2m} k'^2.$$

The Green's function is defined by

$$G_0^{(\pm)}(\boldsymbol{r}, \boldsymbol{r}') = -\frac{\hbar^2}{2m} \langle \boldsymbol{r} | (E_k - \hat{H}_0 \pm i\varepsilon)^{-1} | \boldsymbol{r}' \rangle = \frac{1}{4\pi |\boldsymbol{r} - \boldsymbol{r}'|} e^{\pm ik|\boldsymbol{r} - \boldsymbol{r}'|}$$

((**Proof**))

$$\begin{aligned} I &= -\frac{\hbar^2}{2m} \langle \boldsymbol{r} | (E_k - \hat{H}_0 \pm i\varepsilon)^{-1} | \boldsymbol{r}' \rangle \\ &= -\frac{\hbar^2}{2m} \int\int d\boldsymbol{k}' d\boldsymbol{k}'' \langle \boldsymbol{r} | \boldsymbol{k}' \rangle (E_k - \frac{\hbar^2}{2m} \boldsymbol{k}'^2 \pm i\varepsilon)^{-1} \langle \boldsymbol{k}' | \boldsymbol{k}'' \rangle \langle \boldsymbol{k}'' | \boldsymbol{r}' \rangle \end{aligned}$$

or

$$
\begin{aligned}
I &= -\frac{\hbar^2}{2m}\int\int d\mathbf{k}'d\mathbf{k}''\langle\mathbf{r}|\mathbf{k}'\rangle(E_k-\frac{\hbar^2}{2m}\mathbf{k}'^2\pm i\varepsilon)^{-1}\delta(\mathbf{k}'-\mathbf{k}'')\langle\mathbf{k}''|\mathbf{r}'\rangle \\
&= -\frac{\hbar^2}{2m}\int d\mathbf{k}'\langle\mathbf{r}|\mathbf{k}'\rangle(E_k-\frac{\hbar^2}{2m}\mathbf{k}'^2\pm i\varepsilon)^{-1}\langle\mathbf{k}'|\mathbf{r}'\rangle \\
&= -\frac{\hbar^2}{2m}\int\frac{d\mathbf{k}'}{(2\pi)^3}\frac{e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')}}{E_k-\frac{\hbar^2}{2m}\mathbf{k}'^2\pm i\varepsilon}
\end{aligned}
$$

where

$$E_k=\frac{\hbar^2}{2m}\mathbf{k}^2 .$$

Then we have

$$
\begin{aligned}
I &= -\frac{\hbar^2}{2m}\int\frac{d\boldsymbol{k}'}{(2\pi)^3}\frac{e^{i\boldsymbol{k}'\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{\frac{\hbar^2}{2m}(\boldsymbol{k}^2-\boldsymbol{k}'^2)\pm i\varepsilon} \\
&= \int\frac{d\boldsymbol{k}'}{(2\pi)^3}\frac{e^{i\boldsymbol{k}'\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{k'^2-(k^2\pm i\varepsilon)}=G_0^{(\pm)}(\boldsymbol{r}-\boldsymbol{r}')
\end{aligned}
$$

In summary, we get

$$\langle\boldsymbol{r}|\psi^{(\pm)}\rangle=\langle\boldsymbol{r}|\boldsymbol{k}\rangle-\frac{2m}{\hbar^2}\int d\boldsymbol{r}'G_0^{(\pm)}(\boldsymbol{r},\boldsymbol{r}')\langle\boldsymbol{r}'|\hat{V}|\psi^{(\pm)}\rangle$$

or

$$\langle\boldsymbol{r}|\psi^{(\pm)}\rangle=\langle\boldsymbol{r}|\boldsymbol{k}\rangle-\frac{2m}{\hbar^2}\int d\boldsymbol{r}'G_0^{(\pm)}(\boldsymbol{r},\boldsymbol{r}')V(\boldsymbol{r}')\langle\boldsymbol{r}'|\psi^{(\pm)}\rangle .$$

More conveniently the Lipmann-Schwinger equation can be rewritten as

$$|\psi^{(\pm)}\rangle=|\mathbf{k}\rangle+(E_k-\hat{H}_0\pm i\varepsilon)^{-1}\hat{V}|\psi^{(\pm)}\rangle$$

with

$$\hat{G}_0^{(\pm)} = -\frac{\hbar^2}{2m}(E_k - \hat{H}_0 \pm i\varepsilon)^{-1},$$

and

$$-\frac{2m}{\hbar^2}\hat{G}_0^{(\pm)}\hat{V} = (E_k - \hat{H}_0 \pm i\varepsilon)^{-1}\hat{V}$$

When two operators $\hat{A}$ and $\hat{B}$ are not commutable, we have very useful formula as follows,

$$\frac{1}{\hat{A}} - \frac{1}{\hat{B}} = \frac{1}{\hat{A}}(\hat{B} - \hat{A})\frac{1}{\hat{B}} = \frac{1}{\hat{B}}(\hat{B} - \hat{A})\frac{1}{\hat{A}},$$

We assume that

$$\hat{A} = (E_k - \hat{H}_0 \pm i\varepsilon), \quad \hat{B} = (E_k - \hat{H} \pm i\varepsilon)$$

$$\hat{A} - \hat{B} = \hat{H} - \hat{H}_0 = \hat{V}$$

Then

$$(E_k - \hat{H}_0 \pm i\varepsilon)^{-1} = (E_k - \hat{H} \pm i\varepsilon)^{-1} - (E_k - \hat{H} \pm i\varepsilon)^{-1}\hat{V}(E_k - \hat{H}_0 \pm i\varepsilon)^{-1},$$

or

$$(E_k - \hat{H} \pm i\varepsilon)^{-1} = (E_k - \hat{H}_0 \pm i\varepsilon)^{-1} + (E_k - \hat{H}_0 \pm i\varepsilon)^{-1}\hat{V}(E_k - \hat{H} \pm i\varepsilon)^{-1}.$$

For simplicity, we newly define the two operators by

$$\hat{G}_0(E_k \pm i\varepsilon) = (E_k - \hat{H}_0 \pm i\varepsilon)^{-1}$$

$$\hat{G}(E_k \pm i\varepsilon) = (E_k - \hat{H} \pm i\varepsilon)^{-1}$$

where $\hat{G}_0(E_k + i\varepsilon)$ denotes an outgoing spherical wave and $\hat{G}_0(E_k - i\varepsilon)$ denotes an incoming spherical wave. We note that

$$\hat{G}_0^{(\pm)} = -\frac{\hbar^2}{2m}(E_k - \hat{H}_0 \pm i\varepsilon)^{-1} = -\frac{\hbar^2}{2m}\hat{G}_0(E_k \pm i\varepsilon).$$

Then we have

$$\begin{aligned}\hat{G}_0(E_k \pm i\varepsilon) &= \hat{G}(E_k \pm i\varepsilon) - \hat{G}(E_k \pm i\varepsilon)\hat{V}\hat{G}_0(E_k \pm i\varepsilon)\\ &= \hat{G}(E_k \pm i\varepsilon)[1 - \hat{V}\hat{G}_0(E_k \pm i\varepsilon)]\end{aligned}$$

$$\begin{aligned}\hat{G}(E_k \pm i\varepsilon) &= \hat{G}_0(E_k \pm i\varepsilon) + \hat{G}_0(E_k \pm i\varepsilon)\hat{V}\hat{G}(E_k \pm i\varepsilon)\\ &= \hat{G}_0(E_k \pm i\varepsilon)[1 + \hat{V}\hat{G}(E_k \pm i\varepsilon)]\end{aligned}$$

Then $\left|\psi^{(\pm)}\right\rangle$ can be rewritten as

$$\begin{aligned}\left|\psi^{(\pm)}\right\rangle &= \left|\mathbf{k}\right\rangle + \hat{G}_0(E_k \pm i\varepsilon)\hat{V}\left|\psi^{(\pm)}\right\rangle\\ &= \left|\mathbf{k}\right\rangle + \hat{G}(E_k \pm i\varepsilon)[1 - \hat{V}\hat{G}_0(E_k \pm i\varepsilon)]\hat{V}\left|\psi^{(\pm)}\right\rangle\\ &= \left|\mathbf{k}\right\rangle + \hat{G}(E_k \pm i\varepsilon)\hat{V}(\left|\psi^{(\pm)}\right\rangle - \hat{G}_0(E_k \pm i\varepsilon)]\hat{V}\left|\psi^{(\pm)}\right\rangle\\ &= \left|\mathbf{k}\right\rangle + \hat{G}(E_k \pm i\varepsilon)\hat{V}\left|\mathbf{k}\right\rangle\\ &= [1 + \hat{G}(E_k \pm i\varepsilon)\hat{V}]\left|\mathbf{k}\right\rangle\end{aligned}$$

or

$$\left|\psi^{(\pm)}\right\rangle = \left|\mathbf{k}\right\rangle + \frac{1}{E_k - \hat{H} \pm i\varepsilon}\hat{V}\left|\mathbf{k}\right\rangle.$$

B.2 The higher order Born Approximation

From the iteration, $\left|\psi^{(+)}\right\rangle$ can be expressed as

$$\begin{aligned}\left|\psi^{(+)}\right\rangle &= \left|\mathbf{k}\right\rangle + \hat{G}_0(E_k + i\varepsilon)\hat{V}\left|\psi^{(+)}\right\rangle\\ &= \left|\mathbf{k}\right\rangle + \hat{G}_0(E_k + i\varepsilon)\hat{V}(\left|\mathbf{k}\right\rangle + \hat{G}_0(E_k + i\varepsilon)\hat{V}\left|\psi^{(+)}\right\rangle)\\ &= \left|\mathbf{k}\right\rangle + \hat{G}_0(E_k + i\varepsilon)\hat{V}\left|\mathbf{k}\right\rangle + \hat{G}_0(E_k + i\varepsilon)\hat{V}\hat{G}_0(E_k + i\varepsilon)\hat{V}\left|\mathbf{k}\right\rangle + ...\end{aligned}$$

The Lippmann-Schwinger equation is given by

$$\left|\psi^{(+)}\right\rangle = \left|\mathbf{k}\right\rangle + \hat{G}_0(E_k + i\varepsilon)\hat{V}\left|\psi^{(+)}\right\rangle = \left|\mathbf{k}\right\rangle + \hat{G}_0(E_k + i\varepsilon)\hat{T}\left|\mathbf{k}\right\rangle,$$

where the transition operator $\hat{T}$ is defined as

$$\hat{V}\left|\psi^{(+)}\right\rangle = \hat{T}\left|\mathbf{k}\right\rangle$$

or

$$\hat{T}\left|\mathbf{k}\right\rangle = \hat{V}\left|\psi^{(+)}\right\rangle = \hat{V}\left|\mathbf{k}\right\rangle + \hat{V}\hat{G}_0(E_k + i\varepsilon)\hat{T}\left|\mathbf{k}\right\rangle$$

This is supposed to hold for any $\left|\mathbf{k}\right\rangle$ taken to be any plane-wave state.

$$\hat{T} = \hat{V} + \hat{V}\hat{G}_0(E_k + i\varepsilon)\hat{T}\,.$$

The scattering amplitude $f(\mathbf{k}',\mathbf{k})$ can now be written as

$$f(\mathbf{k}',\mathbf{k}) = -\frac{2m}{\hbar^2}\frac{1}{4\pi}(2\pi)^3\left\langle\mathbf{k}'\right|\hat{V}\left|\psi^{(+)}\right\rangle = -\frac{2m}{\hbar^2}\frac{1}{4\pi}(2\pi)^3\left\langle\mathbf{k}'\right|\hat{T}\left|\mathbf{k}\right\rangle.$$

Using the iteration, we have

$$\hat{T} = \hat{V} + \hat{V}\hat{G}_0(E_k + i\varepsilon)\hat{T} = \hat{V} + \hat{V}\hat{G}_0(E_k + i\varepsilon)\hat{V} + \hat{V}\hat{G}_0(E_k + i\varepsilon)\hat{V}\hat{G}_0(E_k + i\varepsilon)\hat{V} + \ldots$$

Correspondingly we can expand $f(\mathbf{k}',\mathbf{k})$ as follows:

$$f(\mathbf{k}',\mathbf{k}) = f^{(1)}(\mathbf{k}',\mathbf{k}) + f^{(2)}(\mathbf{k}',\mathbf{k}) + f^{(3)}(\mathbf{k}',\mathbf{k}) + \ldots\ldots.$$

with

$$f^{(1)}(\mathbf{k}',\mathbf{k}) = -\frac{2m}{\hbar^2}\frac{1}{4\pi}(2\pi)^3\left\langle\mathbf{k}'\right|\hat{V}\left|\mathbf{k}\right\rangle,$$

$$f^{(2)}(\mathbf{k}',\mathbf{k}) = -\frac{2m}{\hbar^2}\frac{1}{4\pi}(2\pi)^3\left\langle\mathbf{k}'\right|\hat{V}\hat{G}_0(E_k + i\varepsilon)\hat{V}\left|\mathbf{k}\right\rangle,$$

$$f^{(3)}(\mathbf{k}',\mathbf{k}) = -\frac{2m}{\hbar^2}\frac{1}{4\pi}(2\pi)^3\left\langle\mathbf{k}'\right|\hat{V}\hat{G}_0(E_k + i\varepsilon)\hat{V}\hat{G}_0(E_k + i\varepsilon)\hat{V}\left|\mathbf{k}\right\rangle.$$

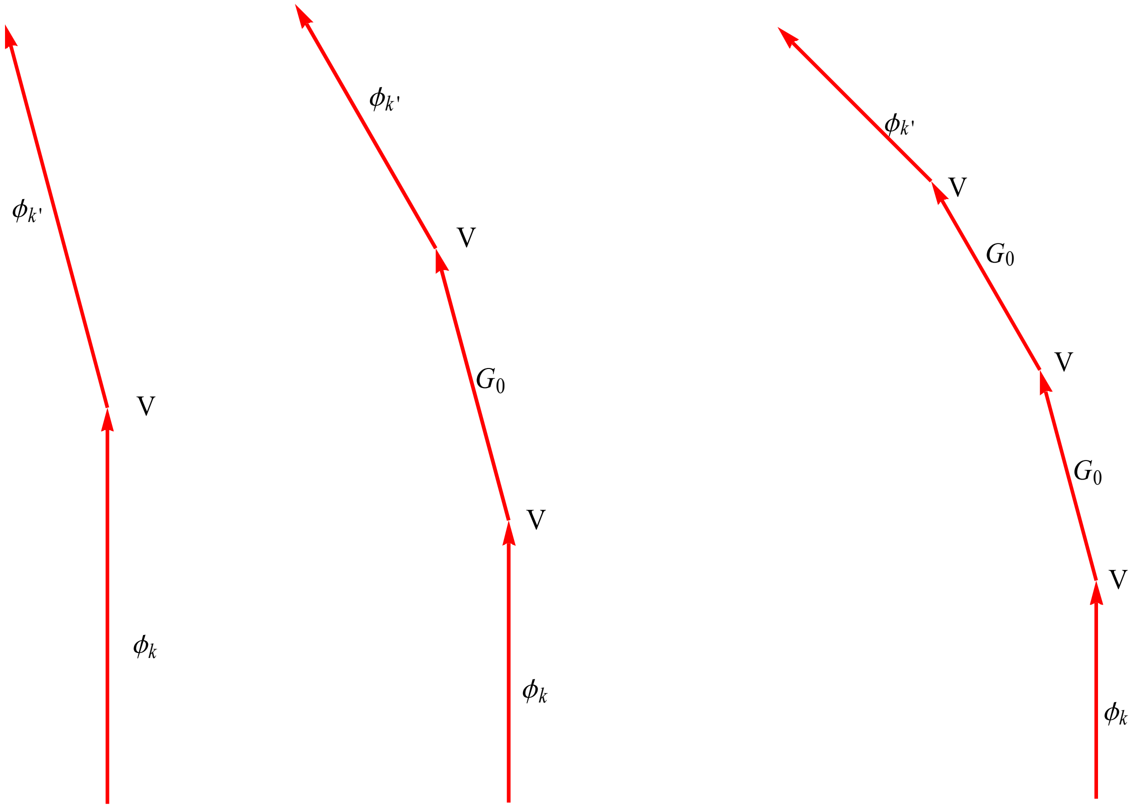


Fig. Feynman diagram. First order, 2nd order, and 3rd order Born approximations. $\phi_k = |\mathbf{k}\rangle$ is the initial state of the incoming particle and $\phi_{k'} = |\mathbf{k'}\rangle$ is the final state of the incoming particle. $\hat{V}$ is the interaction.