NOTE ADDED IN PROOF

When the work for this thesis was completed, and it was in the process of being submitted, two papers appeared in the Physical Review the content of which overlapped in part with the work of Chapters III and IV. G. Toulouse (Phys. Rev. 2 , 270 (July 15,1970)) independently obtained formulae of the type 3.19 and 3.23 for the U infinity limit of the Anderson Hamiltonian. H. Keiter and J.C. Kimball , Phys. Rev. letters 25 , 672(Sept. 7, 1970) , derived a time independent expression for the partition function Z in the Anderson model which is essentially equivalent to the results obtained in Chapter III of the present work. In particular they also succeeded in identifying the graphs which lead to the most divergent contributions to the static susceptibility $\chi(T)$ and obtained the same expression as derived in Chapter IV and given by 4.16 in the U infinity limit.

Thesis entitled :

A PERTURBATION THEORY FOR THE ANDERSON MODEL OF MAGNETIC IMPURITIES IN SIMPLE METALS

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ABSTRACT

The Anderson model of magnetic impurities in simple metals is treated by perturbation theory from two different directions. In both cases, the expansion is carried out in powers of the mixing interaction and the Coulomb repulsion on the impurity is treated exactly. The problem is first approached by using a Green's function method and it is found that the characteristic logarithmic divergence associated with the Kondo effect, cancels in the fourth order, but remains in the sixth order of perturbation theory. Computational difficulties however, seriously restrict the scope of the method, although it does throw some light on some of the more general problems encountered in perturbation treatments of the Anderson model. In the second stage, a time independent expansion is obtained for the Grand Partition Function Z and the Free energy F which simplifies enormously the perturbational calculation of the thermodynamic properties of the system. It is found that by including a certain class of contributions to all orders, a formula is obtained for Z and F which is exact except for contributions of O(1/N) and less. In this way the calculation of Z and F is reduced to solving a self-consistency relation which in the zero temperature limit corresponds to the Brillouin-Wigner formula for the ground state energy shift. Various graphical representations are put forward for the calculation of Z and F by perturbation theory; the limit of an infinitely strong Coulomb coupling leads in particular to a great simplification. With this technique, it has been possible to verify Scalapino's[39] prediction that the dominant contributions to the static susceptibility can be represented by a geometric series. The low temperature limit of the static susceptibility is considered in some detail, both perturbationally and using an 'exact' relation. It is found that in some situations, the two approaches can lead to qualitatively different results.

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CONTENTS

CHAPTER I

INTRODUCTION

Magnetic impurities in metals represent systems of great interest both for their own sake and as a possible means of understanding the magnetism of metals in general. Theoretical work in this direction has been mainly focused on studying the physical properties of a single transition element impurity in a simple metal, that is, a metal in which the electron-electron interactions can to a good approximation be neglected. A typical example of this is afforded by systems corresponding to iron group impurities in noble metals.

Experimental observations on magnetic impurities in different metallic hosts have produced a variety of behaviours for the physical parameters such as the magnetic susceptibility, resistivity ...etc. In particular it has been known for some time that 3d transition metal impurities in some cases give rise to susceptibilities with a Curie like behaviour in simple metallic hosts. This was interpreted by Matthias et al.[1], who performed some of the first experiments that showed this behaviour, as being due to the formation of a localized moment in the region of the impurity. The interesting feature of a metallic host as opposed to an insulator is the itinerant character of the electrons in a metal. Under these circumstances, one expects the interaction between the conduction electrons of the host and the impurity atom to play a significant part in determining the magnetic behaviour of the impurity. The study of such systems will also lead, one hopes, to a better understanding of the processes responsible for ferromagnetism in metals.

To introduce a magnetic impurity i.e an atom which, when isolated, has by Hund's rule a finite spin and orbital angular momentum, into a metallic host is to produce a coupling between the

electrons on the impurity and those of the metal, therefore the existence of a non-vanishing spin in the region around the impurity becomes in practice a cooperative phenomenon. The first summary of the evidence for local moments in simple metals was given by Friedel[2]. Experimentally, by the existence of a local moment one usually means a strongly temperature dependent susceptibility in the form of a Curie law; temperature independent behaviour is taken to signify no magnetic moment. Both these behaviours have been observed[2] for different impurities in a given host, as well as for a given impurity in different hosts.

In practice of course, one never has a single impurity, but a finite even though small concentration, in a given host. One could expect that impurity-impurity interactions should play a significant part. It turns out however that this is not so because though the susceptibility can in many cases be described by a Curie-Weiss law of the form

$$\chi = \frac{C}{\theta + T}$$

the Curie-Weiss constant θ is independent of impurity concentration and cannot therefore be a result of impurity-impurity interactions. Experimentally θ is always finite and the magnetic behaviour is never of the free spin type ($\theta = o$). The data in the magnetic cases such as CuFe (ref.3) and CuMn can be made to fit a law of the type (1.1) with $\theta = -32^{\circ}K$ for the high temperature susceptibility. Measurements carried out down to very low temperatures have however established that the magnetic susceptibility never diverges; this is true for all systems studied so far[3].

Another aspect of the impurity problem which has turned out to be very fruitful in the conceptual understanding of the physical effects that are involved, was the observation of the now well known resistivity minimum in dilute alloys (ref.3). It has been

established that this resistance minimum occurs when the impurity atom is magnetic' (i.e. a strongly T dependent susceptibility). It was shown by Sarachik et al.[4] that there exists a complete correspondence between a strongly temperature dependent susceptibility and the appearance of a resistivity minimum. The weak concentration dependence of the effect indicated that, like the susceptibility, it cannot be due to impurity-impurity interactions, but must be a result of the coupling between the impurity electrons and conduction electrons of the host metal. Kondo's[5] explanation of the resistance minimum in dilute alloys using a model of a magnetic impurity interacting via an s-d exchange mechanism with the conduction electrons of the host, opened up a whole new area for theoretical and experimental activity. Kondo showed by using perturbation theory and going beyond the first Born approximation that the existence of a term proportional to log(T) seemed to lead to good agreement with the experimental behaviour of a variety of systems over a wide temperature range. However the logarithmic term found by Kondo was itself a problem, for it meant the ocurrence of a contribution which would diverge in the limit $T \to o$. In fact it indicated a breakdown in perturbation theory for an antiferromagnetic coupling J at temperatures below a characteristic temperature given by

$$kT_K = W\exp(-1/|J|\,N(o))$$

where W is the band width, k is the Boltzmann constant and N(o) is the density of states at the Fermi level, and where $J < 0$.

This breakdown in perturbation theory was itself a new and interesting phenomenon which had to be explained. Later theoretical work[6] suggested that this divergence was to be associated with the formation of a "quasi bound" state between the localized spin and the conduction electron spin for $J<o$. Nagaoka[6] argued that this spin compensated state appeared to come about gradually as

the temperature was lowered,in other words there was to be no phase transition. Mössbauer[7] and N.M.R.[8] studies at sufficiently low temperatures have provided some evidence in support of the concept of such extended spin correlations. Nevertheless in general the theoretical picture is inconclusive; many questions have to be answered with more authority before it can be claimed that we have a complete understanding of the wide range of observed behaviour.

a) THEORETICAL MODELS

Many properties of dilute alloys have been explained in the past by using the model that an additional potential is produced when an impurity is introduced in the metallic host. Thus the problem was reduced to that of the scattering of the conduction electrons by a single atom in a metal. This was the basis of the approach of Friedel et al.[9] who first introduced the concept of a virtual bound state in a metal,i.e a state resonantly built up from the continuum states and which has a finite lifetime. This concept followed from the observation that the impurity energy levels would in general lie within the conduction band of the host and that therefore these states would not really be localized, because they would acquire a finite lifetime as a result of admixture with the continuum states. The way the question was put with regard to the existence of a local moment was to ask under what conditions is it possible to have an unequal population of 'up' and 'down' spins,on the average, occupying the virtual level.

The theoretical models that have been proposed to describe magnetic impurities in simple metals and on which most attention has been focused in recent times are those of Anderson[10] and Wolff[11]. In the Anderson model one thinks of the impurity as

a localized extra orbital representing the d level of a transition metal atom in an otherwise noninteracting 'electron gas'. This is particularly applicable when the impurity atom has an unfilled or partly filled d shell and the conduction band states of the matrix are s-like. In the case where there is only one unfilled d shell with two possible spin orientations, the Anderson Hamiltonian can be written in the second quantized representation

$$H_A = \sum_{k\sigma} \varepsilon_{k\sigma} n_{k\sigma} + \sum_{\sigma} \varepsilon_{d\sigma} n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + \sum_{k\sigma} V_{dk} (c^+_{k\sigma} c_{d\sigma} + c^+_{d\sigma} c_{k\sigma}) \quad (1.1)$$

The first term represents the kinetic energy of the band states the second is just the unperturbed energy of the d state on an impurity atom. The third term corresponds to the Coulomb repulsion between the up and down spin electrons in the d state. This repulsion is generally assumed to be the most important contribution responsible for the formation of magnetic moments. Clearly it favours occupation of the d level by electrons of either up or down spin. The last term is the so called mixing term, it represents the transfer of electrons from the Bloch states of the conduction band to the impurity state and vice versa. V_{dk} is normally assumed to be independent of $\underline{k}$, which means that only the s waves are affected by the potential. In which case one can write

$$V_{dk} = \frac{v}{\sqrt{N}} = V$$

The Wolff model treats the scattering of the conduction electrons from the impurity by a zero range δ function type potential of the form

$$H_{ps} = V \sum_{kk'\sigma} a^+_{k\sigma} a_{k'\sigma}$$

and the Coulomb repulsion is represented as a repulsion between two electrons of opposite spin which occupy simultaneously the Wannier function located at the impurity site. The Wolff Hamiltonian may be written

$$H_W = \sum_{k\sigma} \varepsilon_{k\sigma} n_{k\sigma} + V \sum_{kk'\sigma} a^+_{k\sigma} a_{k'\sigma} + U n_{o\uparrow} n_{o\downarrow} \qquad (1.2)$$

where

$$U n_{o\uparrow} n_{o\downarrow} = U \sum_{ki} a^+_{k_1\uparrow} a_{k_2\uparrow} a^+_{k_3\downarrow} a_{k_4\downarrow}$$

The Wolff model appears to be more applicable when the states of the impurity are similar to those of the host metal, but despite the formal difference between the Anderson and the Wolff Hamiltonian, the physical situation they describe are the same. Within the framework of approximate theories however, one may in practice turn out to be more convenient than the other. Both models neglect all interactions in the matrix, this seems to be quite justifiable in simple metals such as the noble metals for instance.

The formal simplicity of the Anderson model for example is misleading, the Hamiltonian still represents a many body problem. The Coulomb interaction on the impurity is transferred to the host via the mixing interaction, and the tendency to equal up and down occupation is counteracted by the Coulomb repulsion.

b) THE HARTREE FOCK APPROXIMATION

The Hartree Fock approximation to the Anderson model was orginally carried out by Anderson[10], it is a helpful step conceptually to posing the problem. A very direct way of obtaining Anderson's solution as well as solving the problem in some limiting situations is to use the Retarded Green's function method of Zubarev[12] The retarded Green's function of two operators A and B in the Heisenberg representation is defined by

$$G_{AB}(t-t') = \ll A(t) : B(t') \gg$$
$$= -i\theta(t-t') \langle [A(t), B(t')]_{+-} \rangle$$

where the inner bracket represents either a commutator or anticommutator

and the average is taken over an ensemble..

After taking the Fourier transform with respect to time the equation of motion of the Green's function can be written

$$E\ll A:B\gg_E = 1/2\pi\langle\left[A(0),B(0)\right]_{+-}\rangle + \ll\left[A,H\right]_{-}:B\gg_E \qquad (1.3)$$

where $\ll A:B\gg_E$ is the Fourier transform of $\langle\langle A(t):B(t')\rangle\rangle$ with respect to $(t-t')$.

The equal time correlation functions $\langle AB\rangle$ are expressed in terms of the Green's function by the formula

$$\langle BA\rangle = 2\int_{-\infty}^{\infty}\{-\mathrm{Im}\ll A|B\gg_E\}f(E)dE \qquad (1.4)$$

where $F(E)= \dfrac{1}{e^{\beta E}+1}$ and Im denotes the 'imaginary part of'

For the Anderson Hamiltonian one can immediately set up the following equations of motion, starting with

$$(1/2\pi)G_{kk',\sigma} = \ll c_{k\sigma}\left|c^{+}_{k'\sigma}\right\gg_E \qquad (1.5)$$

$$(E-\varepsilon_k)\,G_{kk'\sigma} = \delta_{kk'} + VG_{dk'\sigma} \qquad (1.6)$$

$$(E-\varepsilon_{k'})G_{dk'\sigma} = VG_{dd,\sigma} \qquad (1.7)$$

from which we obtain the exact relation

$$G_{kk',\sigma}(E) = \frac{\delta_{kk'}}{E-\varepsilon_k} + \frac{V^2 G_{dd,\sigma}(E)}{(E-\varepsilon_k)(E-\varepsilon_{k'})} \qquad (1.8)$$

where V_{dk} has been taken as V and $G_{dd,\sigma}(E) = \ll c_{d\sigma}\left|c^{+}_{d\sigma}\right\gg_E (2\pi)$

equation (1.8) shows that $G_{dd,\sigma}$ acts as the conduction electron t matrix, a knowledge of $G_{dd,\sigma}$ is sufficient to solve the problem completely.

a') U=0

In this limit the problem can be solved exactly, from

$$(E-\varepsilon_{d\sigma})G_{dd\sigma} - V\sum_k G_{kd\sigma} = 1 \qquad (1.9)$$

$$(E-\varepsilon_{k\sigma})G_{kd\sigma} = VG_{dd\sigma} \qquad (1.10)$$

giving

$$G_{dd\sigma}(E) = \frac{1}{E-\varepsilon_{d\sigma} - V^2\sum_k \frac{1}{E-\varepsilon_{k\sigma}}} \qquad (1.11)$$

The sum over k in the self energy of $G_{dd\sigma}$ can be evaluated as follows

$$\lim_{\delta\to 0} \sum_k \frac{V^2}{E-\varepsilon_k + i\delta} = P\sum_k \frac{V^2}{E-\varepsilon_k} - i\pi V^2 g(E)$$

where $g(E)= \sum_k \delta(E-\varepsilon_k)$ and P denotes 'principal part of'. The first term on the R.H.S can be treated as an inconsequential energy shift and can be absorbed by redefining ε_d, g(E) corresponds to the density of states in the conduction band. Assuming $g(E)V^2\pi$ can be treated as a constant Δ, then (1.11) becomes

$$G_{dd\sigma}(E) = \frac{1}{E-\varepsilon_{d\sigma} + i\Delta} \qquad (1.12)$$

The system can be seen to behave as if there were a virtual state at $E = \varepsilon_{d\sigma} - i\Delta$. The resonant nature of the virtual state may be seen from the density of states now given by

$$N_{d\sigma}(E) = -1/\pi \mathrm{Im}\, G_{dd\sigma}(E) \qquad (1.13)$$

$$= 1/\pi \frac{\Delta}{(E-\varepsilon_{d\sigma})^2 + \Delta^2}$$

Δ is identified as the d electron lifetime

b') $V = 0$

Another limiting situation which is of interest specially with reference to Chapter II is the case V =0. In this case we have the two equations

$$(E-\varepsilon_{d\sigma})\, G_{dd\sigma} = 1/2\pi - U \left\langle\!\!\left\langle c_{d\sigma}\, n_{d-\sigma} \,\middle|\, c^+_{d\sigma} \right\rangle\!\!\right\rangle_E \qquad (1.14)$$

$$(E - \varepsilon_{d\sigma} - U) \ll c_{d\sigma} n_{d-\sigma} | c^{+}_{d\sigma} \gg_{E} = 1/2\pi \langle n_{d-\sigma} \rangle \qquad (1.15)$$

The solution is:

$$G_{dd\sigma}(E) = \frac{1 - \langle n_{d-\sigma} \rangle}{E - \varepsilon_{d\sigma}} + \frac{\langle n_{d-\sigma} \rangle}{E - \varepsilon_{d\sigma} - U} \qquad (1.16)$$

In this limit therefore there are two levels corresponding to $E = \varepsilon_{d\sigma}$, and $E = \varepsilon_{d\sigma} + U$, when $2\varepsilon_{d\sigma} + U$ is > 0 (where the energies are measured relative to the Fermi level ε_f) the impurity is singly occupied by either an 'up ' or 'down' spin electron at T = 0.

c)H.F approximation

The Hartree Fock approximation can be obtained by writing the Coulomb term in the form

$$1/2\ U \sum n_{d\sigma} n_{d-\sigma} \longrightarrow \sum_{\sigma} U/2 \left[\langle n_{d\sigma} \rangle n_{d-\sigma} + \langle n_{d-\sigma} \rangle n_{d\sigma} \right]$$

where the averages $\langle n_{d\ \sigma} \rangle$ are to be determined self consistently. In this form, the Coulomb term can be absorbed in H^{o}_{d} where H^{o}_{d} is equal to $\sum_{\sigma} \varepsilon_{d\sigma} n_{d\sigma}$ and by writing instead $\sum_{\sigma} (\varepsilon_{d\sigma} + U \langle n_{d-\sigma} \rangle)\ n_{d\sigma}$

The d electron Green function then simply becomes

$$G_{dd\sigma}(E) = \frac{1}{E - \varepsilon_{d\sigma} - U\langle n_{d-\sigma} \rangle - V^2 \sum_{k} \frac{1}{E - \varepsilon_{k\sigma}}} \qquad (1.17)$$

$$\text{where } \langle n_{d\sigma} \rangle = -1/\pi \int_{-\infty}^{\infty} \mathrm{Im} \left\{ G_{dd\sigma}(E) \right\} f(E) dE \qquad (1.18)$$

$$\text{with } -1/\pi \mathrm{Im}\ G_{dd\sigma}(E) = \frac{1/\pi\ \Delta}{(E - E_{d\sigma})^2 + \Delta^2}, \text{ and } E_{d\sigma} = \varepsilon_{d\sigma} + U\langle n_{d-\sigma} \rangle$$

Equations (1.17) and (1.18) must be solved selfconsistently, at T = 0, we have

$$\langle n_{d\sigma} \rangle = 1/\pi \int_{-\infty}^{0} \frac{\Delta\ d\varepsilon}{\Delta^2 + (E_{d\sigma} - \varepsilon)^2} \qquad (1.19)$$

giving

$$\langle n_{d\uparrow} \rangle = 1/\pi \cot^{-1}\left[(\varepsilon_d + U\langle n_{d\downarrow}\rangle)\Delta^{-1}\right] \qquad (1.20)$$

$$\langle n_{d\downarrow} \rangle = 1/\pi \cot^{-1}\left[(\varepsilon_d + U\langle n_{d\uparrow}\rangle)\Delta^{-1}\right] \qquad (1.21)$$

The details of the selfconsistent solutions are given by Anderson[10] The regions of magnetic and non magnetic behaviour are shown in fig.1), where non magnetic means $\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle$

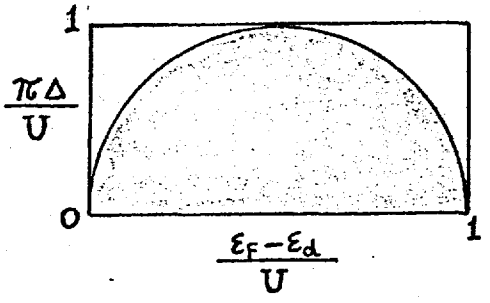


Fig.1. Shaded area represents the region of magnetic behaviour. Ref.(10).

The critical value for moment formation can be expressed by the instability condition

$$\frac{d\langle n_{d\uparrow}\rangle}{d\langle n_{d\downarrow}\rangle} = -1 \qquad (1.22)$$

which leads to

$$U\, N_d(0) = 1 \qquad (1.23)$$

(1.23) has the same form as the Stoner criterion for ferromagnetism[13] The favourable situation for magnetism is

$$\Delta + \varepsilon_d \ll 0 \qquad (1.24)$$

$$\varepsilon_d + U \gg \Delta \qquad (1.25)$$

this may be seen from a simple physical argument: for a magnetic

situation ($\langle n_{d\uparrow}\rangle \neq \langle n_{d\downarrow}\rangle$) one expects that the virtual level must in one case lie well beneath the Fermi level, while in the other case it must lie well above it, thus one level is almost full and the other almost empty.

The Hartree Fock approximation has serious shortcomings, it fails to take into account the d-d correlations on the impurity: it does not treat adequately the correlation in time between the up and down spins on the impurity and therefore tends to overestimate the tendency to moment formation. For the Anderson model, one can physically think of a parameter U/Δ such that when $U/\Delta > 1$ one expects the system to develop a moment and $U/\Delta < 1$ to signify the non magnetic situation. The reason for this can be seen if one notes that Δ the virtual level width is a measure of the inverse of the time a d-electron spends on the impurity, then the longer the electron spends on the impurity (on the average) the more the Coulomb interaction plays a part and thus U/Δ large is favourable to magnetism and vice versa. It is easy to see that the Hartree Fock approximation can only be valid, if at all, in the region $U/\Delta < 1$, i.e when the time spent on the average by a d-electron on the impurity is short compared to U in which case it is conceivable that a self consistent field approach may be adequate. Another serious defect of the H-F solution with regard to the problem of magnetism is the fact that it breaks the rotational invariance of the original Hamiltonian, a manifestation of which is the appearance of a sharp critical boundary between magnetic and non magnetic behaviour (fig.3). This implies a sharp phase transition, a concept which is not expected to be valid for a system consisting of a single impurity in an 'infinite sea of electrons

c) THE EFFECTS OF CORRELATIONS

Various attempts have been made to include in some measure the effects of correlations in the Anderson Hamiltonian. Both perturbational and non perturbational solutions have been proposed. In particular one should mention the work of Hewson[14] and Schrieffer and Mattis[15].

Hewson used a non perturbational approach based on the equations of motion method for the Green's function[12]. He solved the equations using a decoupling scheme which is such that the solution is exact in both limiting situations U= 0 and V= 0. We note that in the Hartree Fock approximation the limit $V \to 0$ of $G_{dd\sigma}(E)$ gives

$$G_{dd\sigma}(E) = \frac{1}{E - \varepsilon_d - U\langle n_{d-\sigma}\rangle} \qquad (1.26)$$

(1.26) is in contrast to the correct solution which is given by (1.16) Hewson concluded that in general the impurity would be nonmagnetic. A similar conclusion was reached by Schrieffer and Mattis[15] using a perturbation theory based on summing the ladder diagrams in the zero temperature linked diagram technique[16]:

In the ladder approximation, the vertex part $T(E_1 + E_2)$ can be written[15]

$$T(E_1 + E_2) = \frac{U}{1 + U\, T^{o}(E_1+E_2)} \qquad (1.27)$$

the approximation is exact for the two body problem, one presumes therefore that it is valid in the limit of low density. Even then, to evaluate the self energy in a simple way, Schrieffer and Mattis had to make an approximation of the Hartree Fock type by assuming that the density of states given by (1.13) could be represented by a Lorentzian. In the Schrieffer Mattis solution, the criterion for magnetism can be written

$$U_{eff} N_d(0) = 1 \qquad (1.28)$$

where $U_{eff} = T(0)$, and $T^{o}(0)$ is given by

$$T^{o}(0) = 1/2\pi i \int_{-\infty}^{\infty} d\varepsilon \; G^{o}_{d\sigma}(\varepsilon) G^{o}_{d-\sigma}(-\varepsilon) \qquad (1.29)$$

$G^{o}_{d\sigma}(\varepsilon)$ corresponds to the result given by (1.11), equation (1.28) follows if one assumes T(E) can be approximated by T(0), in which case the self energy $\sum_{\sigma}(\varepsilon)$ simply becomes

$$\sum\sigma(0) = T(0)\langle n_{d-\sigma}\rangle \qquad (1.30)$$

With (1.30) we are simply back to the H.F type self energy with U replaced by U_{eff}. $U_{eff}N_{d}(0)$ turns out to be generally less than 1 and Schrieffer and Mattis concluded that in the low density limit the ground state of the Anderson Hamiltonian was probably nonmagnetic.

Conceptually the Schrieffer Mattis approach may perhaps be thought of as having contributed to the theory, the picture first introduced by Kannamori[17] for the theory of magnetism in metals, that the effect of correlations in some situations is to produce an effective reduced Coulomb interaction on the impurity. But this is only directly useful within the framework of an 'effective field approach'.

d) THE KONDO EFFECT

A conceptual breakthrough was made by Kondo's[5] discovery of the anomalous logarithmic term in the perturbation expansion of the scattering amplitude of the conduction electrons from the impurity using the so called s-d model. The s-d model was first used by Zener[18] to describe magnetism in metals. It was subsequently used to describe a magnetic impurity in a simple metal and interacting with the conduction electrons of the host via a spin-spin interaction. The model makes the a priori assumption that there is a fixed spin

on the impurity, and in this respect is more phenomenological than the Anderson model. The s-d Hamiltonian is usually written

$$H_{s-d} = \sum_{k} \varepsilon_{k\sigma} n_{k\sigma} - \sum_{k\,k'} J_{kk'} \left[S_z (c^{+}_{k_\uparrow} c_{k'_\uparrow} - c^{+}_{k_\downarrow} c_{k'_\downarrow}) + S^{+} c^{+}_{k_\downarrow} c_{k'_\uparrow} + S^{-} c^{+}_{k_\uparrow} c_{k'_\downarrow} \right] \qquad (1.31)$$

$S^{\mp}$ and S_z are the components of the spin operator associated with the impurity. $J_{kk'}$ is usually taken as independent of $\underline{k}$ and $\underline{k}'$ and is simply replaced by $J/2N$. For $J>0$ the s-d interaction is ferromagnetic and for $J<0$ it is antiferromagnetic.

Kondo showed, using the s-d model that there are processes in higher orders of perturbation theory (beyond the first Born approximation) which give rise to divergent contributions to the scattering amplitude. The divergence is a logarithmic one, at zero temperature and to order J^2 it behaves as $\log|\varepsilon|$ as ε tends to 0. He showed that the resistance minimum found experimentally in dilute alloys could be explained with an antiferromagnetic J. It is well known from scattering theory[19] that divergences in the scattering amplitude are usually associated with the existence of a bound "state". Subsequent theoretical work using variational[20,21] perturbational Green's function[22] and non perturbational techniques,[23,24,25,26] suggested that the logarithmic divergence was associated with the formation of a spin compensated singlet state with extended spin correlations in the region of the impurity.

Kondo[5] showed that the matrix element $T_{k_\uparrow k'_\uparrow}$ for the scattering of an electron from $\underline{k}$ to $\underline{k}'$ in the s-d model is given in lowest order by

$$-J/4N\ S_z$$

In second order there is a scattering that consists of two successive events. First, electron $\underline{k}_\uparrow$ goes to $\underline{k}''_\uparrow$ or $\underline{k}''_\downarrow$ and in the second event $\underline{k}''_\uparrow$ or $\underline{k}''_\downarrow$ is changed to $\underline{k}'_\uparrow$. There is also an analogous

process in second order. The sum of the matrix elements for the two processes and for elastic scattering i.e $\varepsilon_k = \varepsilon_{k'}$, can be written

$$(J/4N)^2 \left[S_z^2 + 1/2(S^+S^- + S^-S^+) \sum_{k''} \frac{1}{\varepsilon_k - \varepsilon_{k''}} \right]$$

$$+ (J/4N)^2 \left[(S^-S^+ - S^+S^-) \sum_{k''} \frac{f_{k''} - 1/2}{\varepsilon_{k''} - \varepsilon_k} \right] \qquad (1.32)$$

The second term is the one leading to the logarithmic divergence and does not vanish because of the noncommutativity of the local spin operators,in fact if we put

$$\sum_{k}' \frac{f_k' - 1/2}{\varepsilon_k - \varepsilon_k} = q(\varepsilon) \qquad (1.33)$$

then $q(\varepsilon)$ behaves as $N(0)\log(\varepsilon/W)$ at $T=0$, which diverges in the limit as $\varepsilon \to 0$ (i.e as it approaches the Fermi level) . It has been assumed that the density of states in the conduction band $N(\varepsilon)$ can be taken as

$$\begin{aligned} N(\varepsilon) &= N(0) \qquad -W \lesssim \varepsilon \lesssim W \\ N(\varepsilon) &= 0 \qquad \text{outside} \end{aligned} \qquad (1.34)$$

At finite temperatures and $\varepsilon = 0$ the divergence in ε is replaced by a divergence in T, $q(\varepsilon)$ is then proportional to[5]

$$N(0)\log(kT/W) + (\text{terms of lower order})$$

The resistivity may be easily calculated in this order, the result can be written

$$R = c\gamma_m \left[1 + N(0)J\log(kT/W) \right] \qquad (1.35)$$

where c is the concentration, γ_m is the first Born scattering term. The logarithmic term is a many body effect associated with the additional internal degree of freedom of the localized spin. The Pauli exclusion principle comes into play in the intermediate

because of the noncommutativity of the localized spin operators. Such an effect does not occur for ordinary potential scattering with a many body sea of electrons in the limit of infinite impurity mass. This point has been considered in detail by Silverstein[27]. Similar logarithmic divergences have been found in the other physical parameters such as the magnetic susceptibility[28], using the s-d model.

Kondo's treatment, despite its success in explaining the resistance minimum effect, revealed that perturbation solutions for the physical parameters were not valid below a characteristic temperature (or Kondo temperature) T_K given by

$$kT_K = W\exp(-1/|J|N(0)) \qquad (1.36)$$

The physical significance of this divergence was in part elucidated by Nagaoka's work[6].

Nagaoka, using the retarded Green's function method of Zubarev, was able to obtain a non perturbational solution by decoupling at some stage the infinite chain of double time Green's functions. He obtained a set of equations which had to be solved selfconsistently. Nagaoka's approximate solution of these equations showed that the Kondo divergence could be interpreted as a quasi bound state between the conduction electron spin and the localized impurity spin for $J<0$. Subsequent theoretical work based on the idea of a 'localized' singlet state for $J<0$, was carried out using the variational technique of minimization of the ground state energy[29,30], they have found ground state energies lower than the 'normal state' by a condensation energy associated with the quasi bound state. In the simplest approximation the condensation energy just corresponds to kT_K given by (1.36).

Nagaoka succeeded in removing the unphysical singularity in the resistivity at $T = 0$, however his solution failed in the region

$T = T_K$, below which the conduction electron states become unstable near the Fermi surface . His solution is therefore restricted to the domain $T > T_K$. Abrikosov[22] made an attempt to describe the situation when $T < T_K$, he developed a special technique to overcome the non commutativity of the spin operators and used the Feynman graph technique for the Green's function. Abrikosov's summation of the most divergent terms in each order although here too succeeded in removing the T=0 singularity, nevertheless did give a resistivity diverging at $T=T_K$ (for $J<0$) which also meant that the equations become unphysical in the region $T \leqslant T_K$.

Hamann and Bloomfield[31] set up an integral equation using Nagaoka's equations[6] and by making simplifications that are valid as far as the logarithmic divergence is concerned, they succeeded in solving Nagaoka's equations exactly. Their solution removes the singularity associated with the Kondo effect at $T=T_K$ for all the physical parameters, which were found to be well behaved for both $J > 0$ and $J < 0$ at all temperatures (T finite). Furthermore Hamann[32] showed that the susceptibility is well behaved in $T < T_K$ and that in the limit as $T \to 0$ and for a spin 1/2, the local spin is <u>almost</u> compensated by the antiparallel conduction electron spin polarization. The good behaviour of the physical parameters in $T < T_K$ is in qualitative agreement with experiment [3], but the precise temperature dependence of the physical parameters is not, in the limit of low temperatures.[3]

Suhl[25] and Suhl and Wong[26] used a non perturbational method for the s-d model based on Chew-Low scattering theory[19]; they too were able to remove the divergences associated with the Kondo effect. Their solution shows strong similarity with that of Hamann and Bloomfield[31,33].

The theories of Suhl and Nagaoka-Hamann-Bloomfield (NHB)

are important in that they show what one would expect on physical grounds, namely that the divergences associated with the Kondo effect can be removed in a treatment that keeps more than simply the leading order logarithmic terms. To what extent the other terms are kept is however not clear for it has been noted [33] that in the s-d model apart from the leading order terms behaving as e.g $(J^{n+1})(\log kT/W)^n$ in the various expansions for the physical parameters, there will in general be lower order terms behaving as $(J^{n+1})(\log kT/W)^s$ where n and s are integers and $n > s$. These 'lower order' terms are clearly not negligeable as T tends to 0. The theories of Suhl and Nagaoka-Hamann-Bloomfield must certainly have included these lower order terms partially to yield results in the region $T \ll T_K$ and $T \sim T_K$, but to what extend they have done so is difficult to tell. Recently, Zittartz [34] and Zittartz and Müller-Hartmann [35] have shown that the exact solution of Nagaoka's equations at T=0 yield results which violate the Mattis singlet ground state theorem [36], Mattis having proved rigorously that the ground state of the s-d Hamiltonian must be a singlet. Clearly therefore the theories of N-H-B are not correct in the region $T \ll T_K$. Zittartz [34] has also shown that in this theory, the cancellation of the local moment is not exact and obtains a susceptibility which eventually diverges as $T \to 0$. This shows that in this limit, the terms not included in the N-H-B theory must play an important part in determining the behaviour of the physical parameters. In any case the Nagaoka equations are based on an equation of motion decoupling scheme the physical meaning of which is difficult to interpret. This is a disadvantage often associated with approximate non perturbative treatments.

The s-d model together with all its implications becomes particularly relevant in the light of the Schrieffer-Wolff canonical transformation of the Anderson Hamiltonian [37]. They showed by

eliminating the mixing term in (1.1) to first order in V_{dk} using a suitably chosen generating function, that the transformed Hamiltonian can be written when (1.24) and (1.25) are satisfied, as

$$H_{S-W} = H_o + H_2$$

where H_2 is well approximated by

$$H_2 = H_{ex} + H_{dir}$$

H_o is the unperturbed Hamiltonian, H_{dir} is just a potential scattering part and is sometimes included in the s-d Hamiltonian as given by (1.31), and H_{ex} can be written

$$H_{ex} = - \sum_{kk'} J_{kk'} (\psi^+_{k'} \underline{S} \psi^+_k) \cdot (\psi^+_d \underline{S} \psi^+_d) \qquad (1.37)$$

where

$$\psi_k = \begin{pmatrix} c_{k\uparrow} \\ c_{k\downarrow} \end{pmatrix} \qquad \psi_d = \begin{pmatrix} c_{d\uparrow} \\ c_{d\downarrow} \end{pmatrix} \qquad \underline{S} = \underline{\sigma}/2$$

and $\underline{\sigma}/2$ are the Pauli spin matrices. The s-d coupling $J_{kk'}$ is given by

$$J_{kk'} = V_{dk'} V_{kd} \left[\frac{1}{\varepsilon_k - \varepsilon_d - U} + \frac{1}{\varepsilon_{k'} - \varepsilon_d - U} - \frac{1}{\varepsilon_{k'} - \varepsilon_d} - \frac{1}{\varepsilon_k - \varepsilon_d} \right] \qquad (1.38)$$

for $\underline{k}$, $\underline{k}'$ close to k_F $J_{kk'}$ can be taken as $J_{k_F k_F}$

$$J_{k_F k_F} = \frac{2UV^2}{\varepsilon_d(\varepsilon_d + U)} = J \qquad (1.39)$$

clearly for $\varepsilon_d < 0$ and $\varepsilon_d + U > 0$, $J < 0$ and the interaction is antiferromagnetic.

It appears therefore that in (1.24) and (1.25) the Anderson Hamiltonian is equivalent to the s-d Hamiltonian. This is certainly true if there are no new physical effects associated

with the terms that have been neglected. But even though this 'equivalence'must be tested in greater detail by future work,one can say immediately that the Anderson model must contain partly the picture predicted by the s-d model. In the light of the Schrieffer-Wolff canonical transformation,both the s-d model and the Anderson model become very interesting indeed , it implies that the Anderson model which is more realistic contains physical effects verified experimentally in the framework of the s-d model. But it also poses the problem of how close the contact is between these models specially in relation to the results and concepts arrived at through the investigation of the s-d model e.g Kondo temperature,localized spin compensated by conduction electron spin polarization,singlet ground state ...etc .

Kondo type divergences in the physical parameters have been found using the Anderson model and making and expansion in V while keeping U exactly,this is of course what one should expect. Hamann[38] found a logarithmic term in the resistivity in order V^6 and in the U infinity limit. The coefficient was found to be in agreement with the result of the s-d model when J is identified via (1.38). Scalapino[39] made an expansion of the Free energy in powers of V and obtained the susceptibility to order V^4 in which order he found a logarithmic term in agreement with the s-d model calculations[28]. However in the techniques used so far,the mathematical difficulties associated with an expansion in powers of V have made it impractical to go beyond the first few orders in perturbation theory. Dworin[40] attempted to devise a technique which would be able to deal with this difficulty,and allow higher order terms to be analyzed. He developed a method based on the equations of motion technique for the double time Green's function[12],his method is however far too complicated for practical purposes.

Perturbation theories for the Anderson Hamiltonian in powers of U and keeping the mixing term exact are easier to carry out to high orders and also have the advantage that one can describe directly the dynamical properties of the impurity spin system, this is because one can employ the usual diagrammatic methods of Field theory[16]. The dynamic susceptibility theories of Lederer and Mills[41] for the Wolff model and Suhl[42] for the Anderson model have made it possible to incorporate in the theory, the concept developed for homogeneous metals by Berk and Schrieffer[43] and Doniach and Engelsberg[44] namely that of 'Spin fluctuations'. The physical picture that has emerged from this approach is that one can think of the impurity as having a moment on a certain time scale, in other words the localized spin moment has a finite lifetime. This is also connected with the more general consideration that the question of whether the impurity is 'magnetic' or 'non magnetic' is itself not well defined. If by magnetic one means that the time average of the occupation number of the impurity states has an unequal population of 'up' and 'down' spins, then this is not really satisfactory because it omits all consideration of the dynamics of the situation. The definitions of magnetic and non magnetic should be related to what one observes experimentally. Then it is much more satisfactory to talk of magnetic as meaning that the lifetime of the moment is sufficiently long so that it is detectable by experiment, but this in turn also depends on whether the particular experiment is measuring the static or dynamical aspects of the localized moment [45]. These ideas have found in the spin fluctuation theory some theoretical basis.

The localized Paramagnon propogator $\chi_d(w)$ or d-electron dynamic susceptibility is generally assumed to be of the form[41]

$$\chi_d(w) = 1/\pi \; \frac{\mu^2}{iw + 1/\tau_{sf}} \qquad (1.40)$$

where τ_{sf} is the spin fluctuation lifetime and w is the 'frequency' . In the limit $\tau_{sf} \to \infty$, $\chi_d(w)$ acquires the simple form corresponding to the dynamic susceptibility of a localized free spin.

Zuckermann and Rivier [46] have evaluated the self energy of the one particle Green's function using a $\chi_d(w)$ as given by (1.40) and have claimed to have found the Kondo effect in the limit $\tau_{sf} \to \infty$. This question together with some of the other theoretical questions associated with the Spin fluctuation model are discussed in Chapter II.

Despite its success in clarifying some of the physical concepts involved in the magnetic impurity problem, the spin fluctuation model does not at the present time rest on solid theoretical foundations, it provides mainly an intuitive description. Neither has it been really able to make contact with the predictions of the s-d model which in many cases seem to be in good agreement with experiment, and which one knows must be a fairly good description of the Anderson model in some limiting situation .

Roughly one can think of three different regions for the ratio U/Δ :

1) $U/\Delta < 1$ in which case the simple Hatree Fock picture may be a good enough description in many situations

2) $U/\Delta \sim 1$ here the spin fluctuation description (in its present form) is more appropriate.

3) $U/\Delta \gg 1$ in this region the s-d model is probably correct.

Experimentally one finds for Iron group impurities in noble metals [45] an estimate for $U/\Delta \sim 10$ which is well within region (3); for Iron group impurities in Aluminium one finds $U/\Delta \sim 2$ again in region (3)

in this case it has been suggested [47] that the non magnetism observed is as a result of the Kondo effect with a high Kondo temperature. It appears that for many,if not most cases of interest the region (3) seems to be appropriate,i.e the s-d picture is applicable. Certainly there seems to be a need to treat the Anderson model from an s-d point of view , this is most directly achieved in the framework of perturbation theory by expanding the mixing term V and keeping the Coulomb term exactly . The techniques that have been used up to now are unsuitable to analyze the higher order effects. However approaching the problem from this direction will undoubtably be able to throw some light on the relationship between the Anderson and the s-d model.

In Chapter III a time independent method is proposed for the expansion of the Grand Partition Function Z and the Free energy F which is capable of going beyond the usual low order approximations in a considerably easier manner than the usual techniques used. A graph representation is derived for F and the results , together with those for the susceptibility are discussed in Chapter IV .

In Chapter II , time dependent perturbation theory for the Anderson model is examined. In particular it is shown how Nagaoka-Abrikosov [6,22] type self energies may be obtained from a Green's function technique for the Anderson model , this is also discussed with reference to the usual expansions in powers of U and Spin fluctuation theory.

CHAPTER II

TIME DEPENDENT PERTURBATION THEORIES

A) THE SPIN FLUCTUATION MODEL

For the Anderson model the two quantities of great interest are usually the one particle 'time Temperature' Green's function and the dynamic susceptibility. The 'time Temperature' Green's function $G^{t,T}_{d\sigma}(w)$ is the Fourier transform of $G^{t,T}_{d\sigma}(t)$ where[16]

$$G^{t,T}_{d\sigma}(t) = -i \langle T\{c_{d\sigma}(t)c^{+}_{d\sigma}(0)\}\rangle \qquad (2.1)$$

The operators are in the Heisenberg representation, T is the usual time ordering operator and the average is over the 'perturbed' ensemble. The poles of $G^{t,T}_{d\sigma}(w)$ give the spectrum of one particle excitations at finite temperature. The scattering cross section of the conduction electrons from the impurity is proportional to $\mathrm{Im}G^{t,T}_{d\sigma}(w)$, and from this it is possible to calculate the resistivity. The dynamic properties of the impurity spin are contained in the response function $\chi_R(w)$ [41] which is the Fourier transform of $\chi_R(t)$ where

$$\chi_R(t) = -i\,\theta(t)\langle\left[S^{+}_{d}(t),S^{-}_{d}(0)\right]\rangle \qquad (2.2)$$

The sqare bracket denotes acommutator, $S^{+}_{d} = c^{+}_{d\uparrow}c_{d\downarrow}$, $S^{-}_{d} = c^{+}_{d\downarrow}c_{d\uparrow}$ and $\theta(t)$ is the usual θ function . In the 'imaginary time ' technique $\chi_R(w)$ is calculated by considering the quantity $\chi_d(\tau)$ given by

$$\chi_d(\tau) = \langle T\{S^{+}_{d}(\tau)S^{-}(0)\}\rangle$$

The function $\chi_R(w)$ describes the response of the local spin to an external magnetic field of frequency w . The techniques most often used to calculate $\chi_d(\tau)$ and $G_{d\sigma}(t)$ are based on the Feynman diagram

or Field theory approach .

The expansion of a general two time Green's function in the imaginary time technique is written[16]:

$$T\langle A(\tau)B(0)\rangle = \frac{1}{\langle S\rangle_0} \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_0^{1/T}\int_0^{1/T}\cdots\int_0^{1/T} d\tau_1 \cdots\cdots d\tau_n \left\langle T\left\{A(\tau)B(0)\right.\right.$$

$$\left.\left. H_{int}(\tau_1)H_{int}(\tau_2)\cdots\cdots\cdots\cdots H_{int}(\tau_n)\right\}\right\rangle_0 \qquad (2.4)$$

where H_{int} can either be taken as

1) H_{int} = Mixing + Coulomb term

2) H_{int} = Mixing term

In case (1) the average $\langle\ \rangle_0$ is over a noninteracting ensemble , whereas in case (2) it is with respect to the Kinetic energy and the Coulomb term in (1.1) . The advantage in the first case is that one may use the usual thermodynamic Wick's theorem and the expansion reduces to summing over all topologically distinct connected graphs. Furthermore it is easy to show that the expansion reduces to one in powers of U only because V may be exactly included in every order by taking the 'bare' propagator in the Fourier transform version of the theory as the Green's function given by (1.11) . In the second case the problem is much more difficult because one cannot apply Wick's theorem for the d-states and as a result the problem acquires considerable complexity . Nevertheless it is of great interest as it represents a very different physical situation to (1). This problem is treated in chapter II section B.

One of the simplest approximations for $\chi_d(w)$ is to consider the sum of the so called particle hole ladder diagrams given by

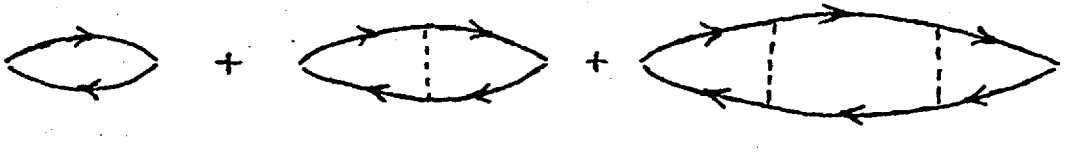
$\chi_d(w) =$  $+\cdots\cdots$

Fig.2

The sum can be written[42]

$$\chi_d(w) = \frac{\chi_B(w)}{1 - U\chi_B(w)} \qquad (2.5)$$

where $\chi_B(w)$ which corresponds to the particle hole bubble is given by

$$\chi_B(w) = -T\sum_{n_1} G^T_{d\sigma}(w + iw_{n_1})G^T_{d-\sigma}(iw_{n_1}) \qquad (2.6)$$

We have written $G^T_{d\sigma}$ for the temperature Green's function in the imaginary time technique. The approximation corresponding to (2.5) is refered to as the R.P.A or time dependent Hartree Fock approximation. It represents the repeated scattering of a particle and a hole pair at the impurity.

The 'zero order' bubble $\chi_B(w)$ may be evaluated by the standard methods of changing the sums over frequencies into integrals[16] and is written as

$$\chi_B(w) = -1/2\pi \int_{-\infty}^{\infty} d\varepsilon \tanh\varepsilon/2T \; \mathrm{Im}G^{t,T}_{dR}(\varepsilon)\left[G^{t,T}_{dR}(\varepsilon+w) + G^{t,T}_{dA}(\varepsilon-w)\right] \quad (2.$$

In (2.7), $G^{t,T}_{dA,R}$ denote the advanced and retarded time Temperature Green's functions respectively.

We note that

$$\mathrm{Re}G_A(w) = \mathrm{Re}G_R(w) = \mathrm{Re}(w) \qquad (2.8)$$

$$\mathrm{Im}G_A(w) = -\mathrm{Im}G_R(w) = \pi N_d(w) \qquad (2.9)$$

where Re and Im denote the real and imaginary parts of respectively. It follows that

$$\mathrm{Re}\chi_B(w) = +1/2\pi \int_{-\infty}^{\infty} d\varepsilon \tanh\varepsilon/2T \; N_d(\varepsilon)\left[\mathrm{Re}(\varepsilon+w) + \mathrm{Re}(\varepsilon-w)\right] \quad (2.10$$

and

$$\mathrm{Im}\chi_B(w) = +\pi/2 \int_{-\infty}^{\infty} d\varepsilon \tanh\varepsilon/2T \; N_d(\varepsilon)\left[N_d(\varepsilon+w) - N_d(\varepsilon-w)\right] \quad (2.11$$

Clearly $\mathrm{Im}\chi_B(w) \longrightarrow 0$ as $w \longrightarrow 0$

further: $\mathrm{Re}\,\chi_B(w)$ at $w = 0$ and at $T = 0$ is given by

$$\mathrm{Re}\,\chi_B(0) = \int_{-\infty}^{0} 2N_d(\varepsilon)\, R(\varepsilon)\, d\varepsilon \qquad (2.12)$$

If G_d^T in $\chi_B(w)$ is taken as the Hartree Fock renormalized propagator and written

$$G^T_{d\sigma}(iw_n) = \frac{1}{iw_n - \varepsilon_{d\sigma} - U\langle n_{d-\sigma}\rangle + i\Delta} \qquad (2.13)$$

where the $\langle n_{d\sigma}\rangle$ have to be evaluated selfconsistently, then with this renormalization we arrive at the analogous result in the Anderson model found for the Wolff model by Lederer and Mills[41] using an equation of motion approach . The static susceptibility $\chi_d(0)$ simply becomes

$$\chi_d(0) = \frac{N_{dH.F}(0)}{1 - UN_{dH.F}(0)} \qquad (2.14)$$

The static susceptibility develops a pole at $1 = UN_{dH.F}(0)$ and perturbation theory breaks down for $UN_{dH.F}(0) \gtrsim 1$, this is simply the Hartree-Fock condition for a local moment to appear (eqn. 1.23). If U_c is is taken as the critical value of U for moment formation in Hatree-Fock theory then for $U \gtrsim U_c$ $\chi_{B\ H.F}(0)$ becomes

$$\chi_{B\ H.F}(0) = -T \sum_{n_1} \frac{1}{U(\langle n_{d\uparrow}\rangle - \langle n_{d\downarrow}\rangle)} \left[G^T_{\uparrow}(i\varepsilon_{n_1}) - G^T_{\downarrow}(i\varepsilon_{n_1}) \right]$$

$$= 1/U \qquad (2.15)$$

Now going back to the more general situation represented by (2.5), we assume, following Lederer and Mills, that for small w the numerator and denominator of (2.5) may be expanded in powers of w as

$$\chi_d(w) \cong \frac{\chi_B(0) + w\chi'_B(0)}{\left[1 - U\chi_B(0)\right] - Uw\chi'_B(0)} \qquad (2.16)$$

where $\chi_B(0)$ denotes $\frac{d}{dw}(\chi_B(w))\Big|_{w=0}$ and only the terms to power w have been kept.

In the non-magnetic situation, it follows easily from (2.7) that Re $\chi_B(0) = 0$ and that Im $\chi_B(0)$ is given by:

$$\text{Im } \chi_B(0) = 1/2\pi \int_{-\infty}^{\infty} d\varepsilon \, \frac{d}{d\varepsilon}\left[\tanh \varepsilon/2T\right] \left[\text{Im } G_d(\varepsilon)\right]^2 \qquad (2.17)$$

which is well approximated by its T=0 limit, $\pi N_d^2(0)$.

Neglecting the second term in the numerator of (2.16), $\chi_d(w)$ becomes :

$$\chi_d(w) = \frac{-\chi_B(0)/U\pi N_d^2(0)}{iw + \dfrac{1 - U\chi_B(0)}{-U\pi N_d^2(0)}} \qquad (2.18)$$

$$= \frac{iA}{w + i\tau} \qquad (2.19)$$

where A is real and $= \dfrac{\chi_B(0)}{U\pi N_d^2(0)}$ and $\tau = \dfrac{1 - \chi_B(0)}{U\pi N_d^2(0)}$

τ can be put $= 1/\tau_{sf}$, where τ_{sf} is interpreted as the spin fluctuation lifetime. In the limit $U\chi_B(0) \to 1$, $\tau_{sf} \to \infty$ i.e. the moment on the impurity becomes infinitely long lived and the system is magnetic in the sense $\langle n_{d\uparrow} \rangle \neq \langle n_{d\downarrow} \rangle$. This situation is allowed to occur in the H.F approximation described above .

In the region $UN_d(0) \sim 1$, τ_{sf}^{-1} may be written $\dfrac{1 - UN_d(0)}{\pi N_d(0)}$.

Equation (2.19) almost sums up spin fluctuation theory. It is the mathematical formulation of the concept that the moment on the impurity must be thought of as existing for a certain ' time ' and is much more

satisfactory than the static 'either' 'or' way of putting the question. On the other hand it may be seen that the form (2.19) is essentially an assumption. It is assumed that the ladder approximation is a good enough description of the response and that furthermore the small frequency limit of the numerator and the denominator of (2.5) is sufficient to describe the dynamical properties of the localized spin. The physical picture that the form (2.19) is designed to give is probably good in the region $U \sim \Delta$ where one can conceive that the low frequency fluctuations of the local moment will be one of the dominant physical effects in determining the behaviour of the physical parameters . The approximation (2.19) having cut out much of the information contained in the dynamic response function .

N.Rivier and M.J.Zuckerman[46] calculated the self-energy contribution to the Green's function $G_d^T(iw_n)$ due to the particle-hole ladder for which the vertex part $\tau_{ph}(w)$ is given by the graphs

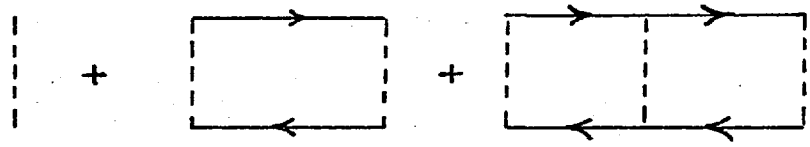
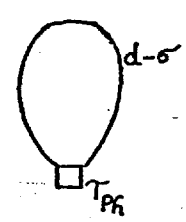
$\tau_{ph}(w) =$  + ...etc.

Fig.3

$$= \frac{U}{1 - U\chi_B(w)}$$

The self-energy $\Sigma_{d\sigma}(w) =$ 

Excluding the first term in the ladder which is simply the H.F term theself-energy can be written as:

$$\Sigma_{d\sigma}(\varepsilon) = TU^2 \sum_n G_{d-\sigma}(\varepsilon - iw_n)\chi_d(iw_n) \qquad (2.20)$$

N.Rivier and M.J.Zuckerman took $\chi_d(w)$ as given by (2,19) and $G^T_{d\sigma}$ as the

Hatree-Fock renormalized propagator (eqn. 2.13). They obtained a self energy the real part of which is proportional to $\ln(4kT/\pi + \tau_{sf}^{-1})$ and argued that in the limit $\tau_{sf} \to \infty$, the self energy acquires the logarithmic behaviour associated with the Kondo effect. We note that in this limit $\chi(iw_n)$ becomes $\frac{iA}{iw_n}$ and

$$\chi_{dA,R}(w) = \frac{iA}{w \pm i\delta} \qquad (2.21)$$

which is similar to the dynamic susceptibility for a free spin, but whereas for a free spin we have

$$\chi^{F}_{A,R}(w) = \frac{n\uparrow - n\downarrow}{w \pm i\delta} \qquad (2.22)$$

in which case the logarithmic self energy cancels in this order because $n_{\uparrow} = n_{\downarrow}$ in zero external field, (2.21) can only be interpreted as a localized spin susceptibility in the region $\langle S_{zlocal} \rangle \neq 0$ but this would be in contradiction to the assumption made in deriving the form (2.19), and it seems doubtful that the logarithmic self energy found in (46) is correctly describing the Kondo effect in the limit $\tau_{sf} \to \infty$. This limit corresponds to the situation where the static susceptibility has a pole and therefore the system exhibits a sharp transition between magnetic and non magnetic behaviour as in H.F theory. Physicallly however, one would not expect the notion of a sharp phase transition to be applicable to a small system such as an impurity, the fluctuations in such a system should be able to smoothen out the sharp critical boundary between magnetic and non magnetic behaviour and the susceptibility should never exhibit a pole. This has been the basis of the approach due to Suhl[42] and Levine and Suhl[48] who have argued that the particle-hole ladder gives the dominant contribution to the dynamic susceptibility and that selfconsistent renormalization of the propogators

in the ladder should remove the pole in the susceptibility which is obtained by the use of unmodified (or H.F modified) propagators. In Suhl's treatment , the equations (2.5) , (2.6) , (2.20) and (2.23) where (2.23) is given by

$$G^{T}_{d\sigma}(iw_n) = \frac{1}{iw_n - \varepsilon_{d\sigma} - V^2\sum_{k}\frac{1}{iw_n-\varepsilon_{k\sigma}} - U\langle n_{d-\sigma}\rangle - \Sigma_d(iw_n)} \qquad (2.23)$$

must be solved selfconsistently . This is in general very difficult and Levine and Suhl[48] further assumed that the low frequency response as described by (2.19) gives the essential features of $\Sigma_d(iw_n)$. Thus in fact what is determined selfconsistently is A, and τ_{sf}. The physical picture that they assumed corresponds therefore to saying that the susceptibility is always close to a pole but that the localized spin fluctuations will always prevent the moment from actually forming in the static sense . Hamann[49] obtained a self-consistent solution to these equations in which the logarithmic effects in the self energy, as in (46) for example, are treated correctly . He also considered the problem in the situation in which these logarithmic effects would be interpreted as the Kondo effect and found that for large U, the characteristic or Kondo temperature T_K in this treatment differs by an enormous factor from the T_K obtained via an s-d treatment of the Anderson model. He concluded that the renormalized R.P.A treatment is not correctly including the Kondo effect. Levine and Suhl[48] also showed that when modified Green's functions are used in the particle-hole ladder, the theory is no longer spin conserving and one has to include a much larger class of diagrams for the susceptibility in order to satisfy the symmetry requirements.

It can be seen that the spin fluctuation picture has not been able to go beyond the 'non magnetic' situation into the s-d type

situation, probably because it has so drastically reduced the physical 'mechanisms' through which this could take place. However the failure to go beyond the small U limit into the large U limit characteristic of the s-d model seems to be rooted in the perturbation method itself. It is very difficult to see how the perturbation expansion in powers of U in its present form could achieve this, to illustrate this point one may consider the expansion when V = 0. (Fig.4)

When V = 0, we know that the exact result for the Green's function is given by (1.16). If this result were to be obtained using the connected graphical expansion for V = 0, the task would a hopeless one.

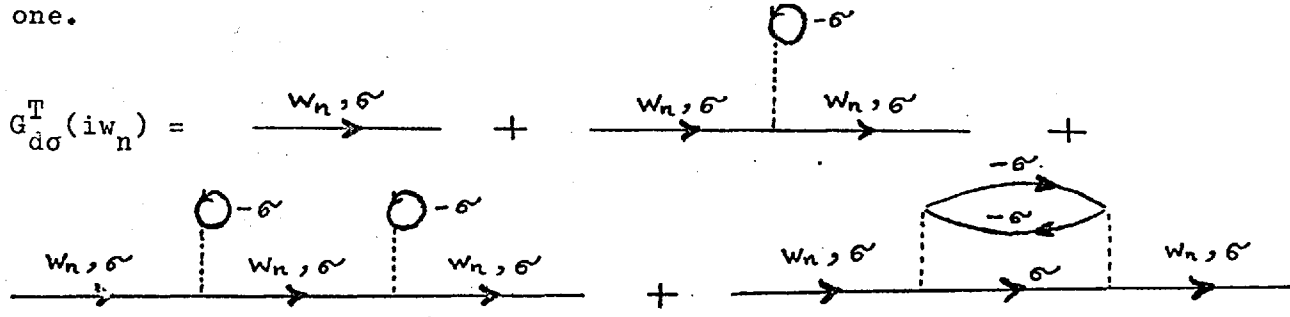


Fig.4

Clearly any partial summation of the above graphs is likely to give a misleading representation for $G^T_{d\sigma}(iw_n)$. The reason for this is not difficult to see; if a direct expansion of (1.16) was made in powers of U and compared with the result of the graphical method, one would note that the latter contains in high orders an enormous class of terms which actually cancel when grouped together in each order and only then does one obtain the contributions of the former. This is of course associated with the application of the thermodynamic Wick's theorem to this problem where all the operators are refering to the same site. As an example of how Wick's theorem works in this case one can consider the average

$$\langle c_{d\sigma} c^+_{d\sigma} n_{d\sigma} n_{d-\sigma} \rangle_0 = (1 - f_{d\sigma}) f_{d\sigma} f_{d-\sigma} - (1 - f_{d\sigma}) f_{d\sigma} f_{d-\sigma} = 0$$

which gives the correct result when both terms are summed as it should do.

In high orders the number of terms on the right hand side will increase considerably, each representing a graph, whereas in fact a tremenduous self cancellation would take place if they were all grouped together. In this way it is easy to see that if only a partial summation is made of these graphs one may obtain a totally irrelevant result, in particular for large U. The difficulty expresses itself in this way that in each individual graph the electrons interact on the d-level as if there were no restriction on the occupation number of the d-level, giving a probabilit f_d and $(1 - f_d)$ for the d-state to be occupied or unoccupied, i.e the Pauli principle is disobeyed in each individual graph. The result (1.16) is trivially simple to derive from perturbation theory if the contributions are evaluated directly and Wick's theorem is not used (see end of section B This difficulty is associated with Wick's theorem in conjunction with partial summations appear less serious when the mixing term is included and the propogators are replaced by those of (1.11) . In this case the impurity level acquires a width Δ and is no longer well localized, but nevertheless it is still there and it is difficult to see how this approach will ever be able to describe the Kondo effect properly and yield the presumably two pole structure of the exact Green's function[40], because in both these cases the correct treatment of the exclusion principle on the d-level is, it seems, essential to produce this structure. These conclusions are supported by the perturbation theory developed in the next section in which U is kept exactly while the expansion is carried out in powers of V.

B) EXACT TREATMENT OF U

In this case H_{int} is taken as

$$H_{int} = V \sum_{k,\sigma} (c^{+}_{d\sigma} c_{k\sigma} + c^{+}_{k\sigma} c_{d\sigma}) \qquad (2.24)$$

and $H_{int}(\tau) = \exp(H_o - \mu N)\tau\ H_{int}\ \exp-(H_o-\mu N)\tau$ (2.25)

where H_o is now given by

$$H_o = \sum_{k,\sigma}\varepsilon_{k\sigma}n_{k\sigma} + \sum_{\sigma}\varepsilon_{d\sigma}n_{d\sigma} + Un_{d\uparrow}n_{d\downarrow} \qquad (2.26)$$

To calculate $G^T_{d\sigma}(\tau_1-\tau_2)$ which is defined as $-1\langle T\{c_{d\sigma}(\tau_1)c^+_{d\sigma}(\tau_2)\}\rangle$ we substitute (2.25) into (2.4) and expand in powers of the mixing interaction. Keeping the terms of order V^2 from the numerator and denominator of (2.4) we have for example:

$$G^T_{d\sigma}(\tau_1-\tau_2) = G^{oT}_{d\sigma}(\tau_1-\tau_2) + \frac{V^2}{2!}(-1)\sum_{k_i\sigma_i}\int_0^{1/T}\int_0^{1/T}d\tau_1 d\tau_2 \Big[\langle T\{c^+_{k_1\sigma_1}(\tau_1)c_{k_2\sigma_2}(\tau_2)\}\rangle$$

$$\langle T\{c_{d\sigma}(\tau_1)c^+_{d\sigma}(\tau_2)c_{d\sigma_1}(\tau_1)c^+_{d\sigma_2}(\tau_2)\}\rangle + \langle T\{c_{d\sigma}(\tau_1)c^+_{d\sigma}(\tau_2)c^+_{d\sigma_1}(\tau_1)c_{d\sigma_2}(\tau_2)\rangle$$

$$\langle T\{c_{k_1\sigma_1}(\tau_1)c^+_{k_2\sigma_2}(\tau_2)\}\rangle + G^{oT}_{d\sigma}(\tau_1-\tau_2)\langle T\{c_{d\sigma_1}(\tau_1)c^+_{d\sigma_2}(\tau_2)\}\rangle$$

$$\langle T\{c^+_{k_1}(\tau_2)c_{k_2}(\tau_1)\}\rangle\Big] \qquad (2.27)$$

The localized and band states are non-interacting and can be decoupled (as shown) in every order, the band states are non-interacting among themselves in H_o and can be expanded by the usual thermodynamic Wick's theorem for 'imaginary times'. The whole difficulty here, is of course that the d-electron many particle Green's functions cannot be expanded by Wick's theorem because H^o includes the Coulomb interaction, but at the same time we do not get into the difficulties mentioned earlier.

One can devise a graphical representation for the terms appearing in the expansion of $G^T_{d\sigma}(\tau_1-\tau_2)$. We represent the 1,2,.... n paricle Green's functions refering to the impurity site merely by a full circle which is the junction of 2,4,.....2n lines carrying the appropriate time, spin indices. The convention used is c_d for an ingoing line and c^+_d for an outgoing line.

e.g $(-1)^2 \langle T\{c_{d\sigma_1}(\tau_1)c^+_{d\sigma_2}(\tau_2)c_{d\sigma_3}(\tau_3)c^+_{d\sigma_4}(\tau_4)\}\rangle$ is represented as (Fig.5)

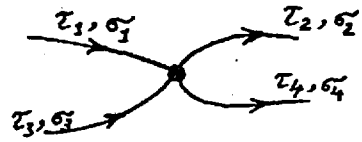


Fig.5

The contribution in each order of the numerator of the expansion for $G^T(\tau_1-\tau_2)$ can then be represented graphically by joining together in all possible ways the internal lines of the n-particle Green's functions by open circles in such a way that an ingoing line is joined to an outgoing line.

e.g to order V^2 the numerator gives

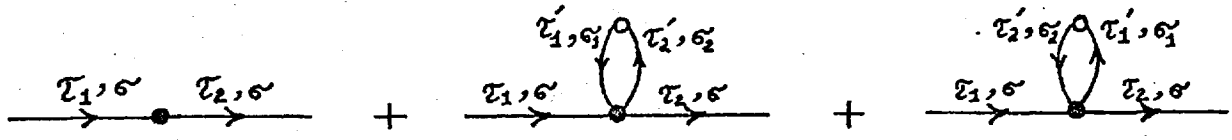


Fig.6

An open circle connecting an ingoing line of index τ_m,σ_m to an outgoing line of index τ_n,σ_n contributes

$$0 \longrightarrow (-1)\langle T\{c_{k_m\sigma_m}(\tau_m)c^+_{k_n\sigma_n}(\tau_n)\}\rangle = G^T_{k_m\sigma_m,k_n\sigma_n}(\tau_m-\tau_n) \qquad (2.28)$$

We sum over all momentum labels, internal spin labels and integrate over all internal time labels. Clearly the two terms of order V^2 graphed (F.6) above give identical contributions, they differ merely by a permutation of the labels. In general to order V^{2n} we have a (n+1)-particle d-Green's function, we join together the 2n internal lines by open circles in all possible ways, there is a symmetry factor $(1/n!)^2$ for each contribution furthermore all the contributions obtained by joining the internal lines in all possible ways are equivalent , there are n! of these. Thus to order V^{2n} there is a single graph in the expansion of the numerator composed of an ingoing and outgoing line into a full circle with n bubbles,

together with a symmetry factor 1/n!.

e.g to order V^4 there is a single graph (Fig.7):

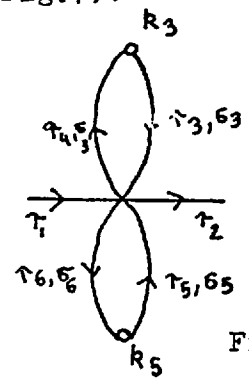


Fig.7

with a symmetry factor 1/2!.

If we choose the convention of writing all the n-particle d-Green's functions as:

$$G^T_{dn}(\tau_1,\tau_2,\tau_3,\ldots\ldots\tau_{2n}) = (-1)^n \langle T\{c_d(\tau_1)c^+_d(\tau_2)c_d(\tau_3)c^+_d(\tau_4)\ldots\ldots c^+_d(\tau_{2n})\}\rangle$$

i.e where an annihilation operator is always followed by a creation operator, and so on, then to a diagram of order V^{2n} there corresponds a factor $(-1)^n$ and a symmetry factor 1/n! where n is the number of bubbles. Clearly $G^T_{k_m k_n}$ may be written $G^T_{k_n\sigma_n}\,\delta_{k_n k_m}\delta_{\sigma_m\sigma_n}$, and thus each bubble has a single spin and momentum index.

Thus to order V^4 for example, the contribution of the numerator graph can be written:

$$\frac{(-1)^2 V^4}{2!}\sum_{\substack{k_3,k_5\\ \sigma_3,\sigma_5}}\int\!\!\int\!\!\int\!\!\int d\tau_3 d\tau_4 d\tau_5 d\tau_6 \Big[G^T_{3d}(\tau_1\sigma,\tau_2\sigma,\tau_3\sigma_3,\tau_4\sigma_3,\tau_5\sigma_5,\tau_6\sigma_5)\, G^T_{k_3\sigma_3}(\tau_3-\tau_4)G^T_{k_5\sigma_5}(\tau_5-\tau_6)\Big]$$

The sum to all orders of the above type graphs, constituted in order V^{2n} of an incoming line and an outgoing line joined to n bubbles, then gives the numerator of the expansion of $G^T_{d\sigma}(\tau_1-\tau_2)$.

The grphs corresponding to the expansion of the denominator i.e $\langle S\rangle_0^{-1}$ in powers of V will give rise to the same kind of diagrams, except that

these will be 'unlinked' , e.g. ,

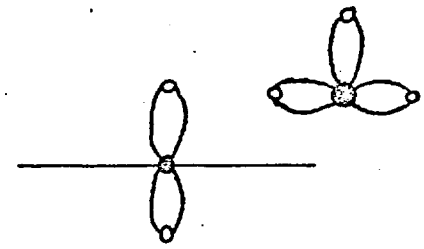


Fig.8 ..... etc.

To a disconnected diagram consisting of a graph with two external lines joined to m bubbles, n_1 vacuum graphs with m_1 bubbles n_2 vacuum graphs with m_2 bubbles,.... n_s vacuum graphs with m_s bubbles there is a symmetry factor $\dfrac{s!}{m!(m_1!)^{n_1}(m_2!)^{n_2}\ldots(m_s!)^{n_s}}$ and a sign factor $(-1)^g(-1)^s$ where g is the total number of bubbles; e.g. the graph (a) of fig. 8 has a factor $(-1)^2(-1)\frac{1}{1!1!}$.

a) Fourier transform

It is simpler to work in the Fourier transform version of the theory . For the imaginary time technique, we write in the usual way[16]

$$(-1)^n \langle T\{c_d(\tau_1)c_d^+(\tau_2)\ldots c_d^+(\tau_n)\}\rangle = T^{2n} \sum_{n_1\ldots n_{2n}} G^T_{dn}(iw_{n_1} iw_{n_2}\ldots iw_{n_{2n}}) e^{-i(w_{n_1}\tau_1 - w_{n_2}\tau_2 \ldots}$$

This relation may be inverted to give:

$$G^T_{dn}(iw_{n_1}, iw_{n_2}, \ldots iw_{n_{2n}}) = \int_0^{1/T} d\tau_1 \ldots \; d\tau_{2n} \; G^T_{dn}(\tau_1, \tau_2, \ldots \tau_{2n}) e^{-i(w_{n_2}\tau_2 - w_{n_1}\tau_1 \ldots)} \qquad (2.30)$$

where $w_n = (i)^{-1}(2n+1)\pi T$, n is an integer and kT has been taken as T throughout. The transform of $G^T_k(\tau_1-\tau_2)$ with respect to the two time variables is easily calculated and is equal to $G^T_k(iw_{n_1}, iw_{n_2})$ where

$$G_k^T(iw_{n_1}, iw_{n_2}) = \frac{1}{iw_{n_1} - \varepsilon_k} \delta_{w_{n_1}, w_{n_2}} \frac{1}{T} \qquad (2.31)$$

Carrying out the appropriate Fourier transformations in the original expansion , the contributions to $G_d^T(iw_n)$ is now evaluated as follows from the graphs: e.g the order V^4 contribution to the numerator (fig.9) becomes

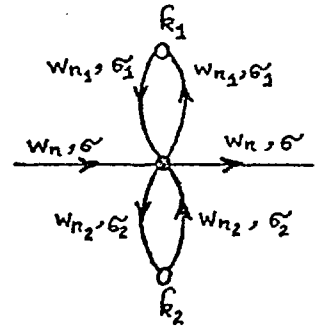


Fig.9

and gives:

$$V^4 \frac{(-1)^2}{2!} T^3 \sum_{\substack{k_1, k_2 \\ \sigma_1, \sigma_2}} \sum_{n_1, n_2} G_{d3}^T(iw_{n\sigma}, iw_{n\sigma}, iw_{n_1\sigma_1}, iw_{n_1\sigma_1}, iw_{n_2\sigma_2}, iw_{n_2\sigma_2}) \times G_{k_1\sigma_1}^T(iw_{n_1}) G_{k_2\sigma_2}^T(iw_{n_2})$$

The problem 'reduces' therefore to evaluating the n-particle Green's functions for the d-electrons in frequency space. This has to be done from first principles by using the definition of the Green's functions and turns out to be impossibly tedious beyond the 2-particle case which is itself very difficult to calculate. In addition to this there is also the difficulty associated with the non-cancellation of the unlinked graphs. This particular difficulty is overcome in the 'cumulant' method or the method developed by Hubbard[50] and which was in particular designed to treat the model often used to describe magnetism in metals. It can equally well be applied to the present perturbation expansion for the Anderson model.

In Hubbard's technique as applied to the Anderson model, the advantage is that one can have a linked cluster theorem. The graphs are

drawn in the same way as before except that the vertices (or full circles) can now be repeated e.g as in the following diagrams

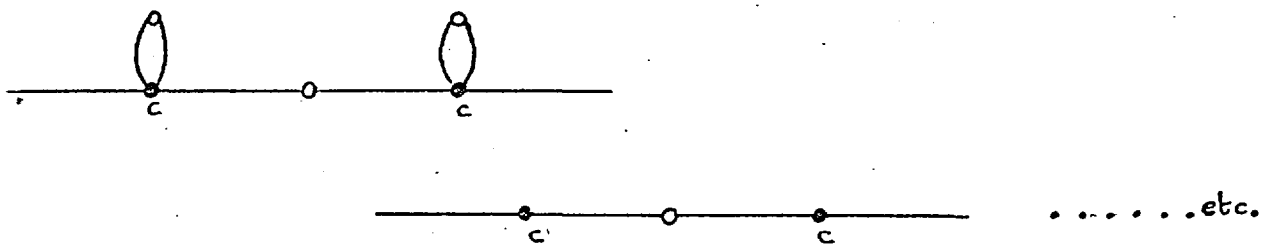


Fig.10

The Green's function is then given by the sum of all topologically distinct connected diagrams, where the vertices can be repeated. In this representation , the full circles no longer denote n-particle Green's functions but the n-particle cumulants defined as follows:

If $A_{\alpha_1}, A_{\alpha_2}, \ldots\ldots A_{\alpha_n}$ refer to Fermi-Dirac operators (in this case they will simply refer to the creation and annihilation operators of the impurity state) , then the cumulant average

$\langle A_{\alpha_1} A_{\alpha_2} \ldots\ldots A_{\alpha_n} \rangle_c$ is defined as

$$\frac{\delta}{\delta\eta_{\alpha_1}(t_1)} \frac{\delta}{\delta\eta_{\alpha_2}(t_2)} \cdots\cdots \frac{\delta}{\delta\eta_{\alpha_n}(t_n)} \log \left\langle \exp\left\{ \sum_\alpha \int_0^{1/\tau} \eta_\alpha(t) A_\alpha(t)\, dt \right\} \right\rangle \Bigg|_{\eta_\alpha(t)=0} \qquad (2.32)$$

where $\eta_\delta(t)\eta_\alpha(t') = -\eta_\alpha(t')\eta_\delta(t)$

The rules for calculating the sign and symmetry factors are given by Hubbard and are particularly complicated. The cumulant method makes it easier to draw all the possible contributions in each order and to make partial summations of diagrams, but the main difficulty associated with the calculation of the d-Green's functions still remains.

As a comparison it is useful to consider the contribution to the Green's function from the direct method and the cumulant method to order V^2.

In the cumulant method there are two graphs in this order:

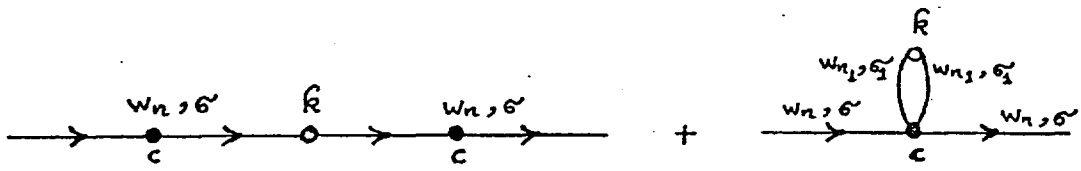


Fig.11

In the direct method we have:

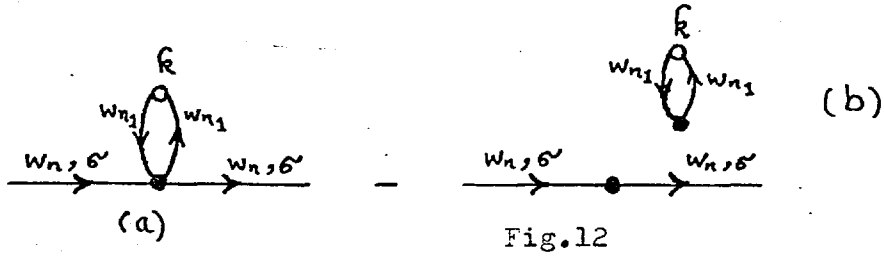


Fig.12

where the index c on the full circle is to distinguish between the cumulant and the Green's function vertices.

The contribution to fig 12 is written:

$$V^2(-1)T^2 \sum_{\substack{n_1,\sigma_1,\\ k_1}} G_d^T(iw_{n\sigma} iw_{n\sigma} iw_{n_1\sigma_1} iw_{n_1\sigma_1}) G^T_{k_1\sigma_1}(iw_{n_1}) + V^2(-1)^2 G^{oT}_{d\sigma}(iw_n) \sum_{\substack{n_1,\sigma_1,\\ k}} G^{oT}_{d\sigma_1}(iw_{n_1}) G^T_{k\sigma_1}(iw_{n_1}) \qquad (2.33)$$

for fig. 11 we obtain:

$$\left[G^{oT}_{d\sigma}(iw_n)\right]^2 V^2 \sum_k G_{k\sigma}(iw_n) + V^2T^2 \sum_{\substack{n_1,\sigma_1,\\ k_1}} G_{k_1\sigma_1}(iw_{n_1}) X_c(iw_{n\sigma}, iw_{n\sigma}, iw_{n_1\sigma_1} iw_{n_1\sigma_1}) \qquad (2.34)$$

Where

$$X_c(\tau_1,\tau_2,\tau_3,\tau_4) = -1 \langle T\{c_d(\tau_1)c_d^+(\tau_2)c_d(\tau_3)c_d^+(\tau_4)\}\rangle - \langle T\{c_d(\tau_1)c_d^+(\tau_2)\}\rangle \langle T\{c_d(\tau_3)c_d^+(\tau_4)\}\rangle - \langle T\{c_d(\tau_1)c_d^+(\tau_4)\}\rangle \times \langle T\{c_d^+(\tau_2)c_d(\tau_3)\}\rangle \qquad (2.35)$$

It is easy to see that when the Fourier transform of (2.35) is substituted back into (2.34), we are back to the expression corresponding to the direct expansion (2.33) as we should expect.

The term $V^2\left[G^{oT}_{d\sigma}(iw_n)\right]^2 \sum_k G_{k\sigma}(iw_n)$ having actually cancelled when grouped together with the 2-particle cumulant graph.

In the cumulant expansion it is already possible at this stage to obtain an approximate expression for $G^T_{d\sigma}(iw_n)$ based on the summation of the graphs

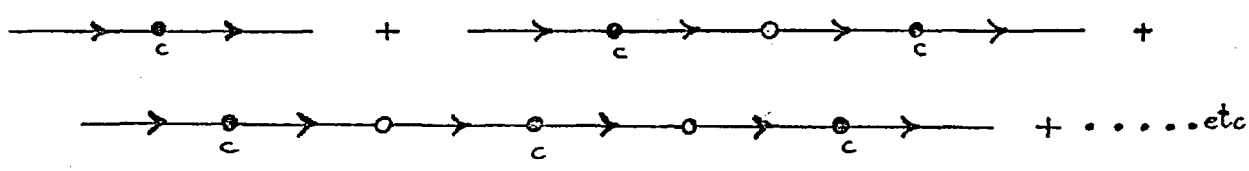


Fig.13

The sum is written

$$G^T_{d\sigma}(iw_n) = \frac{G^{oT}_{d\sigma}(iw_n)}{1 - V^2 G^{oT}_{d\sigma}(iw_n) \sum_k G^T_{k\sigma}(iw_n)} \qquad (2.36)$$

where $G^{oT}_{d\sigma}$ is given by (1.19) with E replaced by iw_n and $G^T_{k\sigma}(iw_n)$ is simply $\frac{1}{iw_n - \varepsilon_{k\sigma}}$ from (2.31) . This approximation gives the correct result in both limits $U \longrightarrow 0$ and $V \longrightarrow 0$. In fact (2.36) is similar to the result obtained by Hewson[14] via an equation of motion method , the difference being that in this case the averages $\langle n_{d\pm\sigma} \rangle$ in $G^{oT}_{d\sigma}$ are zero order , whereas in Hewson's scheme they are to be evaluated self-consistently. Therefore there is no direct connection between the two results .

It was pointed out that the term corresponding to the first expression in (2.34) and to the order V^2 diagram in (2.36) cancelled when the complete contribution was considered, this is actually true in all orders for the diagrams of fig 13. In fact these contributions do not exist when the expansion is written out in full, one has merely added them in one place and substracted them in another. The question that still remains is whether such contributions exist in the direct term corresponding to the first term in (2.33).

If so it must arise when $\sigma_1 = \sigma$. Calculating $G_d^T(iw_{n_1}\sigma, iw_{n_2}\sigma, iw_{n_3}\sigma, iw_{n_4}\sigma)$ from first principles, we obtain

$$G_d^T(iw_{n_1}\sigma, iw_{n_2}\sigma, iw_{n_3}\sigma, iw_{n_4}\sigma) = \frac{(-1)}{\mathrm{Tr}\, e^{-\beta H_d^o}} \left[\mathrm{Tr} \left\{ e^{-\beta H_d^o} \left(\delta_{w_{n_1} w_{n_2}} \delta_{w_{n_3} w_{n_4}} - \delta_{w_{n_1} w_{n_4}} \delta_{w_{n_3} w_{n_2}} \right) \beta^2 \left[\frac{1 - n_{d-\sigma}}{iw_{n_1} - \varepsilon_{d\sigma}} - \frac{n_{d-\sigma}}{iw_{n_1} - \varepsilon_{d\sigma} - U} \right] \left[\frac{1 - n_{d-\sigma}}{iw_{n_3} - \varepsilon_{d\sigma}} - \frac{n_{d-\sigma}}{iw_{n_3} - \varepsilon_{d\sigma} - U} \right] \right\} \right. \tag{2.37}$$

where $\beta = 1/T$, $\delta_{w_n w_{n'}}$ is the Kronecker δ and the $n_{d\pm\sigma}$ in the square brackets are operators.

The result (2.37) is the same as would be obtained by applying Wick's theorem, the difference being however that in this case the $n_{d\pm\sigma}$ are operators and the Trace must be evaluated for the whole product. This result is quite general, the n-paricle Green's functions with all the spins parallel may be expanded by 'Wick's theorem' keeping the $n_{d\pm\sigma}$ as operators and evaluating the Trace with respect to the complete product. If the contribution is now evaluated using the Green's function (2.37) we have the two graphs

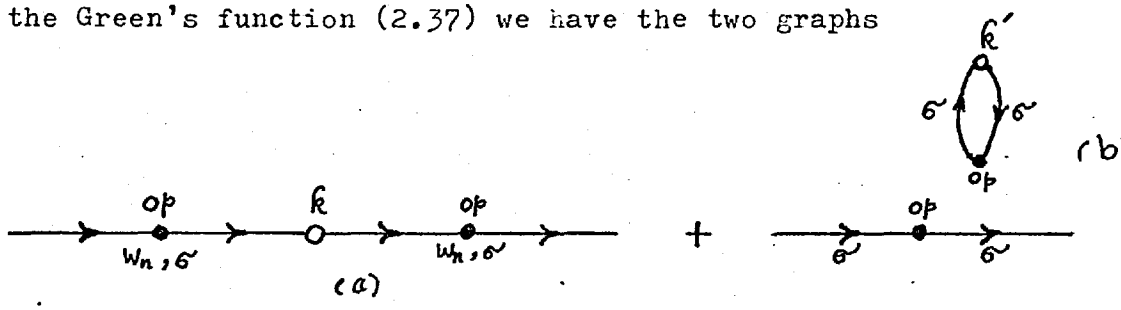


Fig.14

i.e the graph from fig 12a with $\sigma_1 = \sigma$ has broken up into a linked and unlinked graph. The 'op' label signifies that the Trace must be evaluated for the whole product. The linked part contributes:

$$V^2 < \left[G^T_{d\sigma, op}(iw_n) \right]^2 > \sum_k G^T_{k\sigma}(iw_n) \tag{2.38}$$

(2.38) can be rewritten

$$\left[\frac{1-\langle n_{d-\sigma}\rangle}{(iw_n-\varepsilon_{d\sigma})^2}-\frac{\langle n_{d-\sigma}\rangle}{(iw_n-\varepsilon_{d\sigma}-U)^2}\right]V^2\sum_k G^T_{k\sigma}(iw_n) \qquad (2.39)$$

For $\sigma=\sigma_1$ there is in this order another contribution, coming from the expansion of the denominator e.g the second term in (2.33) for $\sigma=\sigma_1$. Combining this with the contribution due to fig.(14b), we have

$$V^2\sum_k G^T_{k\sigma}(iw_n)\left\{\sum_{n_1}\left[G^{oT}_{d\sigma}(iw_n)G^{oT}_{d\sigma}(iw_{n_1})-G^{oT}_{d\sigma,op}(iw_n)G^{oT}_{d\sigma,op}(iw_{n_1})\right]\right\} \qquad (2.40)$$

The analogous term to the first term of (2.34) is clearly (2.38) and is obviously very different from it. Thus it can be seen that the advantage in form gained by the cumulant expansion may be lost in practice when one wishes to carry out partial summations: the above example shows how one could be summing effects which do not actually exist in the complete expansion. The difficulty is similar to the one mentioned in connection with the linked graphical expansion in powers of U at the end of section A.

Working with the direct expansion it can be seen that one can think of two kinds of 'unlinked graphs', those appearing in the expansion of the numerator and those coming from the denominator. The characteristic feature of these unlinked graphs is that they will give rise to contributions having factors of $1/T$, $1/T^2$...etc and must $\longrightarrow 0$ as $T\to 0$. There is good reason to believe that they can be included as renormalizations of the temperature averages, this point is discussed further at the end of this section.

The analogous series to (2.36) in the direct expansion is:

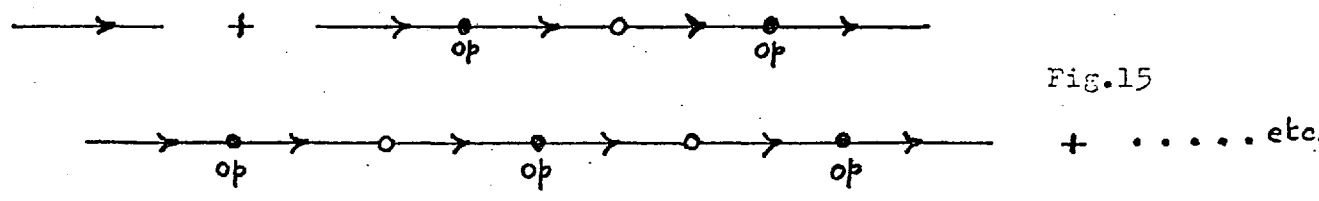


Fig.15

giving

$$G^T_{d\sigma}(iw_n) = \frac{1 - \langle n_{d-\sigma}\rangle}{iw_n - \varepsilon_{d\sigma} - V^2\sum_k \frac{1}{iw_n - \varepsilon_{k\sigma}}} + \frac{\langle n_{d-\sigma}\rangle}{iw_n - \varepsilon_{d\sigma} - U - V^2\sum_k \frac{1}{iw_n - \varepsilon_{k\sigma}}} \qquad (2.41)$$

(2.41) describes two resonances around ε_d and ε_d+U with a width Δ This result can also be obtained from an equation of motion approach, the difference here too is that in the latter the averages are self-consistent whereas here they are zero order. In (2.41) , $G^T_{d\sigma}$ retains its zero order two pole structure , a result strongly suggested for the exact Green's function from an equation of motion analysis[40] and in sharp contrast to Hartree-Fock and renormalized R.P.A type results[49].

To be able to go further with this perturbation approach, one needs to know $G^T_{2d}(iw_{n_1}\sigma, iw_{n_2}\sigma, iw_{n_3}-\sigma, iw_{n_4}-\sigma)$ as well as the higher order Green's functions. These are in general very difficult to compute and it is worthwile to look at some zero temperature results to get an insight into the structure of the higher order Green's functions for finite temperature.

b) Zero temperature

At T=0 we define the one particle Green's function $G^t_{d\sigma}(t-t')$

$$G^t_{d\sigma}(t-t') = (-i)\langle\varphi|T\, c_{d\sigma}(t)c^+_{d\sigma}(t')|\varphi\rangle$$

where the average is taken over the exact ground state $|\varphi\rangle$ of the perturbed system and will be simply denoted by $|\rangle$.

The Fourier transform with respect to t,t' may be written

$$G^t_{d\sigma}(w,w') = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dt\, dt'\, G^t_{d\sigma}(t,t')\, e^{iwt-iw't'}$$

and

$$G^t_{d\sigma}(t,t') = (1/2\pi)^2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dw\, dw' G^t_{d\sigma}(w,w')\, e^{-iwt+iw't'}$$

In general we define the n-particle Green's function at zero temperature as

$$G^t_{dn}(t_1,t_2,t_3,\ldots t_{2n}) = (-i)^n \langle \varphi | T\{c_d(t_1)c^+_d(t_2)\ldots c^+_d(t_{2n})\}|\varphi\rangle \quad (2.42)$$

where as before a c^+ always follows a c and so on .

$$G^{t,\alpha}_d(t-t) = \frac{(-i)}{\langle S(\infty)\rangle}\sum_{n=0}^{\infty}\frac{(-i)^n}{n!}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}dt_1\,dt_2\ldots\ldots dt_n$$
$$\langle T\{c_{d\sigma}(t)c^+_{d\sigma}(t)H_{int}(t_1)\ldots.H_{int}(t_n)\}\rangle_{o,\alpha} \quad (2.43)$$

Where $|\rangle_{o,\alpha}$ denotes one of the 4 possible unperturbed "ground states" given by

$$|\rangle_{o,\alpha} \longrightarrow \begin{cases} |d_\uparrow d_\downarrow\rangle\varphi_F \longrightarrow \alpha_4 \\ |d_\downarrow 0\rangle\varphi_F \longrightarrow \alpha_3 \\ |d_\uparrow 0\rangle\varphi_F \longrightarrow \alpha_2 \\ |0\ 0\rangle\varphi_F \longrightarrow \alpha_1 \end{cases}$$

where φ_F denotes the unperturbed Fermi sphere.

The contributions to $G^{t,\alpha}_{d\sigma}$ may be graphed in the same way as before. For the numerator graphs the contributions are changed accordin to:

$$G^T_{d\sigma}(iw_n,\ldots) \longrightarrow G^t_{d\sigma}(w,\ldots)$$

$$T^{m+1}\sum_{n_1\cdots n_m} \longrightarrow \frac{1}{(2\pi)^{m+1}}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}dw_1\ldots.dw_m$$

and $G^t_{k\sigma}(w) = \dfrac{1}{w - \varepsilon_{k\sigma} + i\delta sing(\varepsilon_{k\sigma})}$

e.g in order V^2 the graph

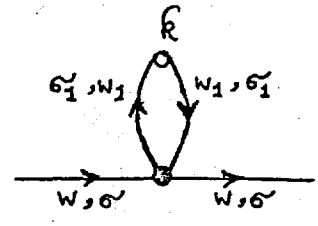


Fig.16

contributes:

$$(-1)V^2(1/2\pi)^2\int_{-\infty}^{\infty}dw_1\sum_{\tilde{\sigma}_1,k}G^t_d(w_\sigma,w_\sigma,w_{1\sigma_1},w_{1\sigma_1})G^t_{k\sigma_1}(w_1)$$

To obtain the full order V^2 result at T=0, one has to evaluate the 2-particle Green's function $G_d^{t,\alpha}(w_{1\sigma}, w_{2\sigma}, w_{3-\sigma}, w_{4-\sigma})$ where α refers to the 4 possible ground states . The $G^{t,\alpha}$ can be found by taking the limit $T \to 0$ of the 'time Temperature ' Green's functions defined in the same way except that the averages are taken over the 'ensemble' of states at finite temperatures. An explicit calculation of $G_2^{t,T}$ gives (Appendix 1)

$$G_d^{t,T}(w_{1\sigma}, w_{2\sigma}, w_{3-\sigma}, w_{4-\sigma}) = \Bigg[(-i)^2 \, \mathrm{Tr} \Bigg\{ e^{-\beta H_d^0} \, \frac{(1-n_{d\sigma})(1-n_{d-\sigma})\delta(w_4-w_3)\delta(w_1-w_2)2\pi i}{(w_1 - \varepsilon_{d\sigma} + i\delta)(w_3 - \varepsilon_{d-\sigma} + i\delta)}$$

$$+ \frac{n_{d\sigma}(1-n_{d-\sigma})\delta(w_1-w_2)\delta(w_3-w_4)}{(w_2 - \varepsilon_{d\sigma} - i\delta)(w_3 - \varepsilon_{d-\sigma} - U + i\delta)} + \frac{n_{d\sigma}n_{d-\sigma}\delta(w_4-w_3)\,\delta(w_1-w_2)}{(w_1 - \varepsilon_{d\sigma} - U - i\delta)(w_3 - \varepsilon_{d-\sigma} - U - i\delta)}$$

$$+ \frac{n_{d-\sigma}(1-n_{d\sigma})\delta(w_1-w_2)\delta(w_3-w_4)}{(w_1 - \varepsilon_{d\sigma} - U + i\delta)(w_3 - \varepsilon_{d-\sigma} - i\delta)} +$$

$$\frac{(1-n_{d\sigma})(1-n_{d-\sigma})\,\delta(w_1+w_3-w_2-w_4)\;(w_2 + w_4 - 2\varepsilon_d)\;U}{(w_1 - \varepsilon_{d\sigma} + i\delta)(w_2 - \varepsilon_{d\sigma} + i\delta)(w_3 - \varepsilon_{d-\sigma} + i\delta)(w_4 - \varepsilon_{d-\sigma} + i\delta)}$$

$$\frac{(1/-2\pi i)}{(w_2 + w_4 - 2\varepsilon_d - U + i\delta)}$$

$$+ \frac{n_{d\sigma}n_{d-\sigma}\,\delta(w_2+w_4-w_3-w_1)\;U(w_2 + w_4 - 2\varepsilon_d - 2U)}{(w_1 - \varepsilon_{d\sigma} - U - i\delta)(w_2 - \varepsilon_{d\sigma} - U - i\delta)(w_3 - \varepsilon_{d-\sigma} - U - i\delta)}$$

$$\frac{(1/-2\pi i)}{(w_4 - \varepsilon_{d-\sigma} - U - i\delta)(w_2 + w_4 - 2\varepsilon_d - U - i\delta)} +$$

$$\frac{n_{d\sigma}(1-n_{d-\sigma})\;\delta(w_2 + w_4 - w_1 - w_3)}{(w_1 - \varepsilon_{d\sigma} - i\delta)(w_2 - \varepsilon_{d\sigma} - i\delta)(w_3 - \varepsilon_{d-\sigma} - U + i\delta)(w_4 - \varepsilon_{d-\sigma} - U + i\delta)}$$

$$\frac{U(w_4 - w_1 - U)\;(1/-2\pi i)}{(w_4 - w_1 + \varepsilon_{d\sigma} - \varepsilon_{d-\sigma} + i\delta)} +$$

$$\frac{n_{d-\sigma}(1-n_{d\sigma})\;\delta(w_2 + w_4 - w_1 - w_3)\;U(w_2 - w_3 - U)\;(1/-2\pi i)}{(w_1 - \varepsilon_{d\sigma} - U + i\delta)(w_2 - \varepsilon_{d\sigma} - U + i\delta)(w_3 - \varepsilon_{d-\sigma} - i\delta)(w_4 - \varepsilon_{d-\sigma} - i\delta)(w_2 - w_3 + \varepsilon_{d-\sigma} - \varepsilon_{d\sigma} + i\delta}\Bigg]$$

×···→

$$\times\left[\frac{(2\pi i)^2}{\mathrm{Tr}\ e^{-\beta H_a}}\right] \qquad (2.44)$$

The result for $G_2^{t,T}$ given by (2.44) is easy to interpret in the limit $T\to 0$. In this limit and in the region $\varepsilon_d > 0$, $2\varepsilon_d + U > 0$ (all the energies are measured relative to the Fermi level) $G_2^{t,T}$ becomes G_2^{t,α_1} which is given by

$$G_{2d}^{t,\alpha_1}(w_{1\sigma},w_{2\sigma},w_{3-\sigma},w_{4-\sigma}) = (2\pi)^2\,\delta(w_1-w_2)\delta(w_3-w_4)G_{d\sigma}^{t,\alpha_1}(w_1)G_{d-\sigma}^{t,\alpha_1}(w_3)$$
$$+\ G_{d\sigma}^{t,\alpha_1}(w_1)\,G_{d\sigma}^{t,\alpha_1}(w_2)\,G_{d-\sigma}^{t,\alpha_1}(w_3)\,G_{d-\sigma}^{t,\alpha_1}(w_4)\,T_{pp}(w_2+w_4)\,(2\pi)\delta(w_2+w_4-w_1-w_3)$$

where

$$G_{d\sigma}^{t,\alpha_1}(w) = \frac{1}{w - \varepsilon_{d\sigma} + i\delta} \qquad \text{and } T_{pp}(w+w_1) = \frac{iU(w + w_1 - 2\varepsilon_d)}{(w + w_1 - 2\varepsilon_d - U + i\delta)} \qquad (2.45)$$

G_2^{t,α_1} can be represented

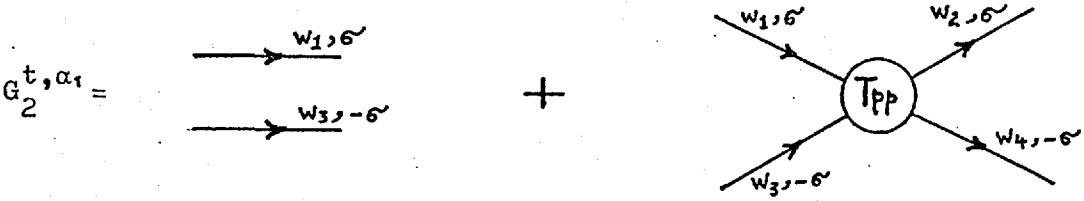


Fig.17

$T_{pp}(E)$ is just the vertex part for the particle-particle ladder. This result could of course have been anticipated because in the region $\varepsilon_d > 0$, $2\varepsilon_d + U > 0$, the only nonvanishing graphs are the ladder graphs and the propogator remains the bare propdgator

$$\frac{1}{w - \varepsilon_d + i\delta\,\mathrm{sing}(\varepsilon_d)} \longrightarrow \frac{1}{w - \varepsilon_d + i\delta}$$

in a perturbation calculation of G_2^{t,α_1} in powers of U.

Similarly, for $\varepsilon_d < 0$, $2\varepsilon_d + U < 0$ we have

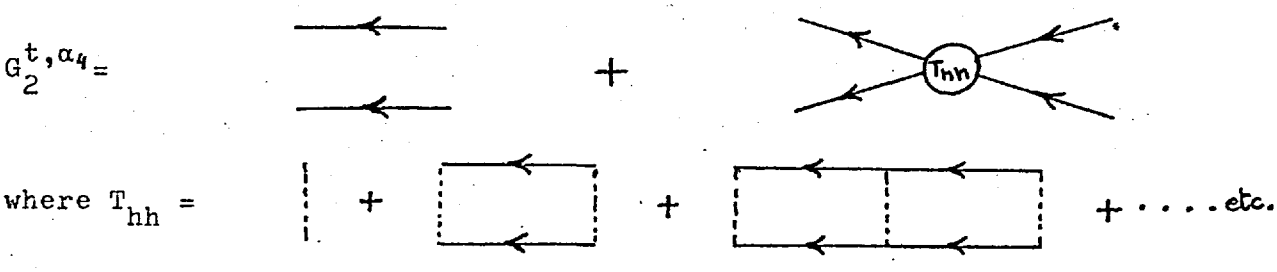
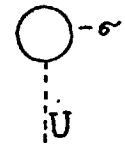


Fig.18

the propagators are $\frac{1}{w - \varepsilon_d - U - i\delta}$ and $T_{hh} = \frac{iU(w_1 + w_3 - 2\varepsilon_d)}{w_1 + w_3 - 2\varepsilon_d - U - i\delta}$

represents the hole-hole ladder. The propagators are renormalized with the Hartree-Fock bubble



which in T=0 and $\varepsilon_d < 0$, $2\varepsilon_d + U < 0$ just gives U.

In the region $\varepsilon_d < 0$, $2\varepsilon_d + U > 0$ the ground state is doubly degenerate , if one takes either $|d_\uparrow 0\rangle \varphi_F$ or $|d_\downarrow 0\rangle \varphi_F$ to be the ground state (in which case one has to think of a small magnetic field lifting the degeneracy), then we have

$G_2^{t,\alpha_i}(w_{1\uparrow}, w_{2\uparrow}, w_{3\downarrow}, w_{4\downarrow}) =$

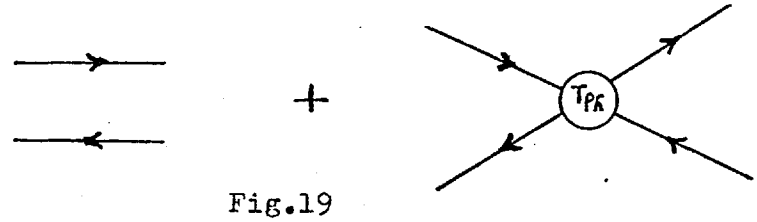


Fig.19

where $G_{d\uparrow}^{t,\alpha_1}(w) = \frac{1}{w - \varepsilon_d - i\delta}$ and $G_{d\downarrow}^{t,\alpha_2}(w) = \frac{1}{w - \varepsilon_d - U + i\delta}$.

$T_{ph}(w_4 - w_1) =$

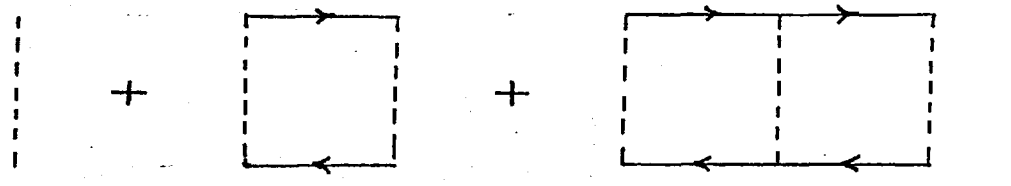


Fig.20

$$= \frac{iU(w_4 - w_1 - U)}{w_4 - w_1 + \varepsilon_{d_\uparrow} - \varepsilon_{d_\downarrow} + i\delta} \qquad (2.46)$$

Similarly of course if $|d_\downarrow 0\rangle \varphi_F$ is taken to be the ground state except for the changes $\uparrow$ to $\downarrow$ and $w_1 \to w_3$, $w_2 \to w_4$.

The graphs for $G_{d\sigma}^{t,\alpha}(w)$ can now be broken up in this order into the more conventional type of representation by identification with the results of a U and V expansion (note that the Green's function to be calculated now also carries a label "α" denoting the unperturbed

state with respect to which the expansion is carried out) .

Thus for $G_d^{t,\alpha_1}(w)$ the order V^2 graph for opposite spins splits up according to

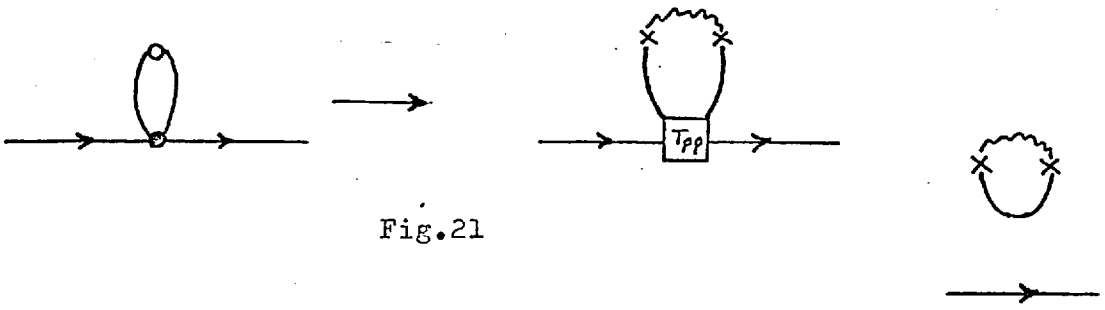


Fig.21

where the wavy line represents $\dfrac{1}{w - \varepsilon_{k\sigma} + i\delta\,\mathrm{sing}(\varepsilon_{k\sigma})}$.

The result to order V^2 for $G_{d\sigma}^{t,\alpha_1}$ and $G_{d\sigma}^{t,\alpha_4}$ is now simply evaluated and only the linked graphs in the usual representation (fig.21) need be considered, the unlinked graphs from the numerator exactly cancel those from the expansion of the denominator in (2.43). The result shows no Kondo type anomaly in this order.

The region of greatest interest is $\varepsilon_d < 0$, $2\varepsilon_d + U > 0$, as one should expect. The scattering properties of the conduction electrons in this region are actually described by $\dfrac{G_{d\sigma}^{t,\alpha_2} + G_{d\sigma}^{t,\alpha_3}}{2}$ as a result of the degeneracy of the ground state. This is easy to see if one imagines taking the limit $T \to 0$ in the finite T case .

The contribution to $G_{d\uparrow}^{t,\alpha_2}(w)$ from the graph

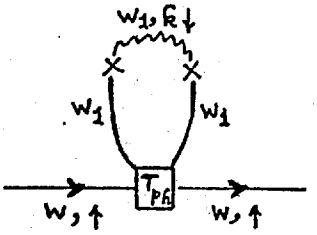


Fig.22

is $= \left[G_{d\uparrow}^{t,\alpha_2}(w)\right]^2 \sum_d(w)$ where $\sum_d(w)$ is given by:

$$\Sigma_d(w) = V^2(1/2\pi)\sum_k \int_{-\infty}^{\infty} dw' T_{ph}(w-w')\left[G_{d\downarrow}^{t,\alpha_2}(w')\right]^2 G_{k\downarrow}^{t}(w') \tag{2.47}$$

$$= V^2 \sum_k \frac{U(w + U - \varepsilon_k)}{w - \varepsilon_k - i\delta} \frac{f_k}{(\varepsilon_k - \varepsilon_d - U)^2} \tag{2.48}$$

in the limit $U \to \infty$ (2.48) becomes

$$\Sigma_d(w) = V^2 \sum_k \frac{f_k}{w - \varepsilon_k - i\delta} \tag{2.49}$$

P $\Sigma_d(w)$ is proportional to $\log|w|$ and is divergent as $w \to 0$.

Similarly for $G_{d\uparrow}^{t,\alpha_3}(w)$ we have

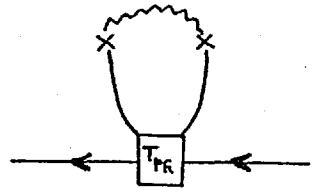


Fig.23

which gives $\Sigma_d(w)\left[G_{d\uparrow}^{t,\alpha_3}(w)\right]^2 = \frac{1}{(w - \varepsilon_d - U + i\delta)^2} \Sigma_d(w)$

and in $U \to \infty$ $$\Sigma_d(w)\left[G_{d\uparrow}^{t,\alpha_3}(w)\right]^2 = V^2 \sum_k \frac{1 - f_k}{(\varepsilon_k - \varepsilon_d)^2(w - \varepsilon_k)} \tag{2.50}$$

(2.50) is also anomalous in the limit $w \to 0$.

The total contribution to $\frac{(G_{d\uparrow}^{t,\alpha_2} + G_{d\uparrow}^{t,\alpha_3})}{2}$ to order

V^2 may then be written:

$$\frac{(G_{d\uparrow}^{t,\alpha_2} + G_{d\uparrow}^{t,\alpha_3})}{2} = \frac{1}{(w - \varepsilon_d)^2} V^2 \sum_k \frac{1}{w - \varepsilon_k} + \frac{(1/2)}{w - \varepsilon_d} + V^2 \sum_k \frac{(1/2)(1 - f_k)}{(w - \varepsilon_d)(\varepsilon_k - \varepsilon_d)^2} + V^2 \sum_k \frac{(1/2)(1 - f_k)}{(w - \varepsilon_d)^2(\varepsilon_k - \varepsilon_d)} \tag{2.51}$$

Thus to this order the anomalous logarithmic terms cancel, but it is

already possible at this stage to draw some interesting conclusions. First one may note the similarity between the particle-hole vertices

(2.46) $\dfrac{1}{w - w' + \varepsilon_{d\uparrow} - \varepsilon_{d\downarrow} \pm i\delta}$ with that of the spin fluctuation theory in the limit $\tau_{sf} \longrightarrow \infty$ (2.21) $\dfrac{iA}{w - w' \pm i\delta}$. This result suggests that the limit $\tau_{sf} \longrightarrow \infty$ describes a similar situation and one should expect the anomaly to cancel in this order as shown by (2.51) . Secondly one can see through the identification of these vertices for the 4 possible 'ground states' with the perturbation expansion in powers of U, that the zero energy transfer particle-hole vertices (2.46) only occur in the region $\varepsilon_d < 0$, $2\varepsilon_d + U > 0$ in the general n-particle Green's functions . It is also clear that in $\varepsilon_d > 0$, $2\varepsilon_d + U > 0$ (or $\varepsilon_d < 0$, $2\varepsilon_d + U < 0$) the only vertices are of the particle-particle type (2.45) (or hole-hole), for which no anomalous behaviour occurs in any order of perturbation theory when the contributions are evaluated.

The Kondo anomalies are to be expected in order V^6 for $G^t_{kk'}(w)$ (or V^4 for $G^{t,\alpha}_d(w)$) . For this in general a knowledge of the 3-particle Green's function is required. From a knowledge of G^t_2 however, it is possible to generate higher order graphs. To see this in a general way and also to show that the unlinked graphs in the expansion of the numerator and denominator exactly cancel in every order in the T=0 method, it is simplest to go back to the cumulant expansion. At T=0 , the temperature averages simply become averages over the 'ground state', furthermore the cumulants (2.32) are in this limit simply identifiable as the completly connected part of the n-particle Green's functions when the latter have been evaluated and graphed as in e.g (2.45), fig 17.

In G^t_3 for example, we know that there will be terms with

1,2,3 energy conservation factors $\delta(w.....)$, G_3^t can be drawn

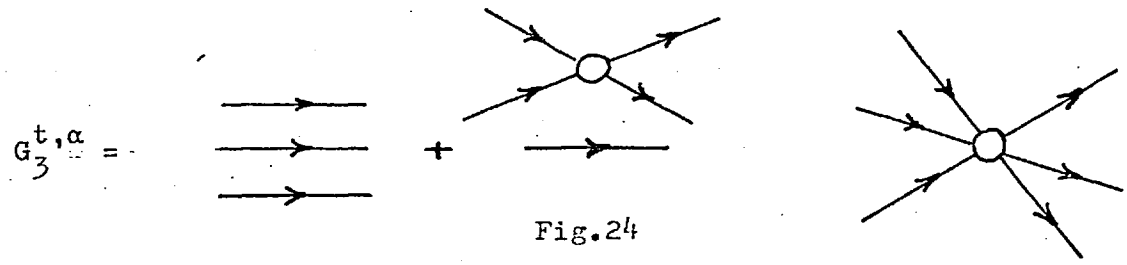


Fig.24

The last term represents the completely cnnected term and has only one energy conservation factor namely $\delta(w_1+w_3+w_5-w_2-w_4-w_6)$ this term is actually equivalent to the 3-particle cumulant crresponding to $G_3^{t,\alpha}$ and calculated by (2.32). Thus at T=0 it is possible and convenient to use the cumulant method, in which case the cumulants are simply the 1,2,.....n particle connected parts as illustrated above, and they may be repeated in all topologically non-equivalent ways. From a knowledge of $G_1^{t.\alpha}$, $G_2^{t,\alpha}$ it is possible for example to construct the following higher order graphs

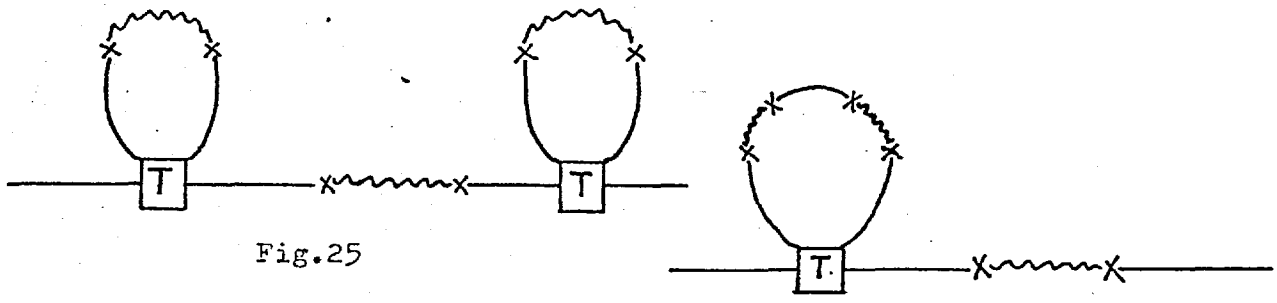


Fig.25

The previous conclusion is really quite obvious, the only reason one needs to use the cumulant argument at all is to generalize it in a simple manner. An additional simplification which may be obtained in a simple way without having to evaluate the higher order Green's functions explicitly, is to deduce the Higher order vertices on the basis of a knowledge of the 2-particle ones and by using the relationship between these results and the perturbation expansion in powers of U. For example it is easy to see that for $\alpha=\alpha_1$ there will be a 3-particle vertex of the type:

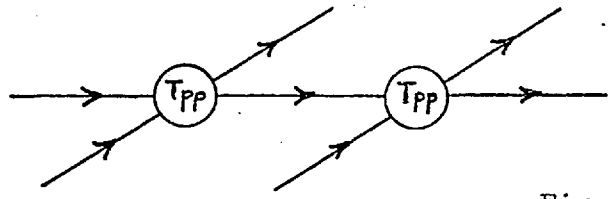


Fig.26

where T_{pp} is given by (2.45) . Thus we may write:

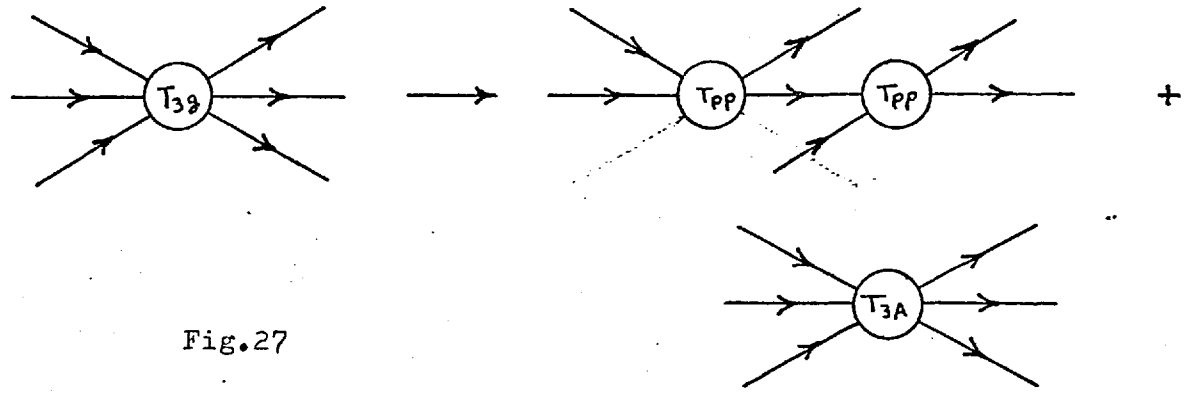


Fig.27

Where T_{3g} refers to the complete 3-particle vertex and T_{3A} refers to those not included in the one which was generated. Unfortunately it is not possible it seems to deduce in this way the complete higher order Green's functions, but nevertheless a considerable number of vertices may be deduced in this way. An explicit calculation of G_3^{t,α_1} gives:

$$G_d^{t,\alpha_1}(w_{1\sigma},w_{2\sigma},w_{3-\sigma},w_{4-\sigma},w_{5-\sigma},w_{6-\sigma}) = (2\pi)^3\ G_{d\sigma}^{t,\alpha_1}(w_1)G_{d-\sigma}^{t,\alpha_1}(w_3)G_{d-\sigma}^{t,\alpha_1}(w_5)$$

$$\left[\delta(w_1-w_2)\delta(w_3-w_4)\delta(w_5-w_6) - \delta(w_1-w_2)\delta(w_3-w_6)\delta(w_5-w_2)\right] \cdots +$$

$$G_{d\sigma}^{t,\alpha_1}(w_1)G_{d\sigma}^{t,\alpha_1}(w_2)G_{d-\sigma}^{t,\alpha_1}(w_3)G_{d-\sigma}^{t,\alpha_1}(w_4)G_{d-\sigma}^{t,\alpha_1}(w_5)G_{d-\sigma}^{t,\alpha_1}(w_6)\left[T_{pp}(w_1+w_3)T_{pp}(w_2+w\right.$$

$$\left.\delta(w_1+w_3+w_5-w_2-w_4-w_6)\ (1/2\pi)^2 + (1/2\pi)^2\delta(w_1+w_3+w_5-w_2-w_4-w_6)\cdot\right] \times\cdot\cdot$$

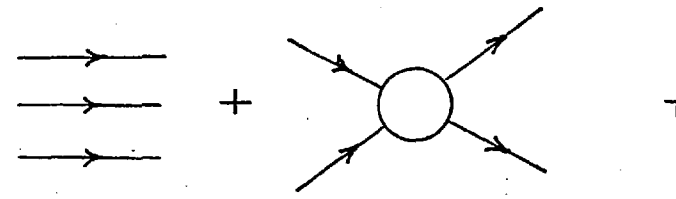
$$\times \frac{U^3}{(w_1 + w_3 - 2\varepsilon_d - U + i\delta)(w_2 + w_4 - 2\varepsilon_d - U + i\delta} \quad +(-1)^P \text{ permutations } \ldots.$$

$\cdots\cdots w_3 \longrightarrow w_5\ ,\ w_4 \longrightarrow w_6$ (P= number of permutations)$\Big]$

$$+\ G^{t,\alpha_1}_{d\sigma}(w_1)G^{t,\alpha_1}_{d\sigma}(w_2)G^{t,\alpha_1}_{d-\sigma}(w_3)G^{t,\alpha_1}_{d-\sigma}(w_4)G^{t,\alpha_1}_{d-\sigma}(w_5)\Big[(1/2\pi)\,\delta(w_5-w_6)T_{pp}(w_1+w_3)$$

$$\delta(w_1+w_3-w_2-w_4) \quad + (-1)^P \text{permutations } w_3\longrightarrow w_5\ ,\ w_4\longrightarrow w_6\Big] \qquad (2.52)$$

Thus G^{t,α_1}_3 =



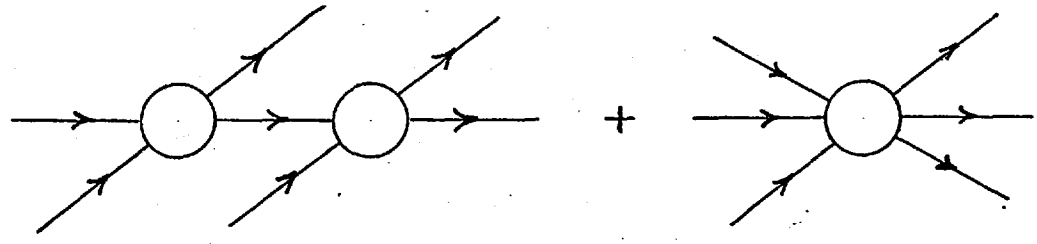


Fig.28

The general 3-particle Green's function has broken up as expected and where everything but the last graph (second part of second term in 2.52) was generated from G^{t,α_1}_2 . Similarly for the other regions corresponding to the 3 other values of α and for the higher order Green's functions.

With (2.52), it is straightforward to evaluate the contribution to $G^{t,\alpha_1}_{d\sigma}$ in order V^4 exactly, it is not difficult to see that there will be no anomalies in this or higher orders as mentioned before. The singlet symmetry of the ground state does not allow the spin flip processes in the intermediate states responsible for the Kondo effect. (similarly for G^{t,α_4}_1 for which G^{t,α_4}_3 may be deduced by simple permutations)

In $\epsilon_d < 0$, $2\epsilon_d + U > 0$, and for $G^{t,\alpha_2}_{d\uparrow}$ we may write down immediately on the basis of the previous discussion, the following set of graphs

$G_{d\uparrow}^{t,\alpha_2}$ =

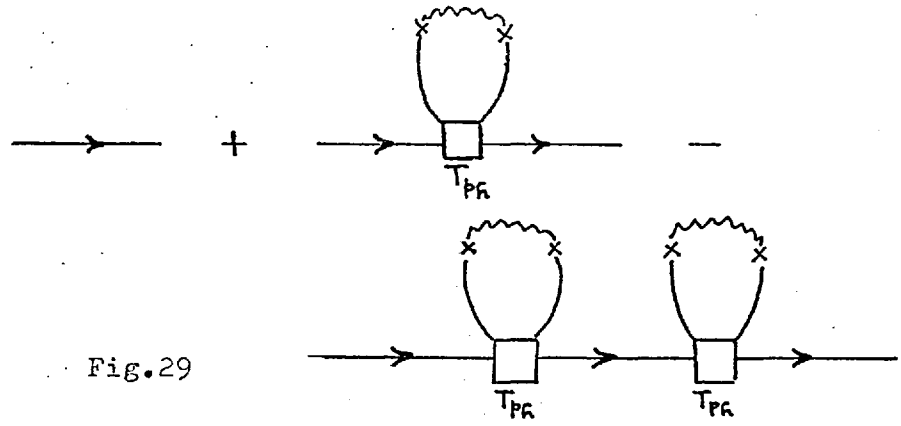
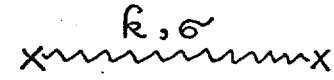


Fig.29

involving the anomalous self energy (2.48) , the above series can be summed to give in $U \longrightarrow \infty$:

$$G_{d\uparrow}^{t,\alpha_2}(w) = \frac{1}{w - \varepsilon_d - V^2 \sum_k \frac{f_k}{w - \varepsilon_k}} \qquad (2.53)$$

including in addition the self energy 

(2.53) becomes

$$G_{d\uparrow}^{t,\alpha_2}(w) = \frac{1}{w - \varepsilon_d - V^2 \sum_k \frac{f_k + 1}{w - \varepsilon_k}} \qquad (2.54)$$

at finite U we can simply use (2.48).

There is an analogous series for $G_{d\uparrow}^{t,\alpha_3}$ giving

$$G_{d\uparrow}^{t,\alpha_3}(w) = \frac{1}{w - \varepsilon_d - V^2 \sum_k \frac{1}{w - \varepsilon_k} - V^2 \sum_k \frac{(1-f_k)(w-\varepsilon_k-U)U}{(w-\varepsilon_k)(\varepsilon_k-\varepsilon_d)^2} - U} \qquad (2.55)$$

(2.55) tends to zero as $U \longrightarrow \infty$.

However it is really $\frac{(G_{d\uparrow}^{t,\alpha_2} + G_{d\uparrow}^{t,\alpha_3})}{2}$ one is interested in. The exact result in order V^4 may be found by using the 3-particle Green's function , in $U \longrightarrow \infty$

$$G_3^{t,\alpha_3}(w_{1\uparrow},w_{2\uparrow},w_{3\uparrow},w_{4\uparrow},w_{5\downarrow},w_{6\downarrow}) = (2\pi)\Big[\delta(w_1+w_3+w_5-w_2-w_4-w_6)\; G_{d\downarrow}^{t,\alpha}(w_6)$$

$$G_{d\downarrow}^{t,\alpha}(w_5)\; G_{d\downarrow}^{t,\alpha}(w_5+w_3-w_2)\quad \frac{1}{(w_1 - w_6 + \varepsilon_{d_\downarrow} - \varepsilon_{d_\uparrow} + i\delta)(w_2 - w_5 + \varepsilon_{d_\downarrow} - \varepsilon_{d_\uparrow} + i\delta)}$$

$$+ \quad (-1)^P \text{permutations} \quad w_1 \longrightarrow w_3\,, \quad w_2 \longrightarrow w_4\Big] \qquad (2.56)$$

$$G_d^{t,\alpha_2}(w_{1\uparrow},w_{2\uparrow},w_{3\uparrow},w_{4\uparrow},w_{5\downarrow},w_{6\downarrow}) = (2\pi)^2\Big[\Big\{(-i)\;\delta(w_3+w_5-w_4-w_6)\delta(w_1-w_2)$$

$$G_{d\uparrow}^{t,\alpha}(w_3)\; G_{d\uparrow}^{t,\alpha}(w_1)\; G_{d\uparrow}^{t,\alpha}(w_4)\quad \frac{1}{w_5 - w_4 + \varepsilon_{d_\uparrow} - \varepsilon_{d_\downarrow} + i\delta} \quad +$$

$$(-1)^P \text{ permutations} \quad w_1 \longrightarrow w_3\,, \quad w_2 \longrightarrow w_4\Big\} \quad - \quad \Big\{(1/2\pi)\delta(w_1+w_3+w_5-w_2-w_4-w_6)$$

$$G_{d\uparrow}^{t,\alpha}(w_3)\; G_{d\uparrow}^{t,\alpha}(w_2)\; G_{d\uparrow}^{t,\alpha}(w_4+w_2-w_3)\quad \frac{1}{w_6 - w_3 + \varepsilon_{d_\uparrow} - \varepsilon_{d_\downarrow} + i\delta}$$

$$\frac{1}{w_5 - w_4 + \varepsilon_d - \varepsilon_d + i\delta} \quad + \quad (-1)^P \text{ permuations} \Big\} \quad - \quad \Big\{(1/2\pi)$$

$$\delta(w_1+w_3+w_5-w_2-w_4-w_6)\; G_{d\uparrow}^{t,\alpha}(w_2)\; G_{d\uparrow}^{t,\alpha}(w_4)\; G_{d\uparrow}^{t,\alpha}(w_1)\; G_{d\uparrow}^{t,\alpha}(w_4+w_2-w_3)$$

$$\frac{1}{w_5 - w_4 + \varepsilon_{d_\uparrow} - \varepsilon_{d_\downarrow} + i\delta} \quad + \quad (-1)^P \text{ permutations} \quad w_1 \longrightarrow w_3\,, \quad w_2 \longrightarrow w_4\Big\}\Big] \qquad (2.57)$$

The general finite U result could have been obtained by making appropriate transformations in (2.52) .

The particular spin arrangements chosen in (2.57) are actually sufficient to obtain all the relevant possibilities in the general fourth order term. In this order the anomalous terms do not cancel and in fact make a contrbution to $\mathrm{Im}\dfrac{(G_{d\uparrow}^{t,\alpha_2} + G_{d\uparrow}^{t,\alpha_3})}{2}$

proportional to $\sum_k \frac{1 - 2f_k}{w - \varepsilon_k}$ which behaves as $\log|w|$ as $w \to 0$.

c) Finite temperatures

The two particle temperature Green's function G_2^T must be closely related to the 2-particle time temperature Green's function given by equation (2.44). There are in principle general relations connecting these functions similar to those for the one particle case[16], however these can be very complicated and it is more convenient to evaluate it directly (Appendix 2). Thus we have in $U \to \infty$:

$$
\begin{aligned}
G_2^T(w_{n_1\sigma}, w_{n_2\sigma}, w_{n_3-\sigma}, w_{n_4-\sigma}) = {} & \frac{(-1)^2}{\mathrm{Tr}\, e^{-\beta H_d^o}} \Big[\mathrm{Tr} \Big\{ e^{-\beta H_d^o} \quad (1 - \delta_{w_{n_4}, w_{n_1}}) \\
& \delta_{w_{n_1}+w_{n_3}, w_{n_2}+w_{n_4}} (1/T) \quad \frac{n_{d-\sigma}(1 - n_{d\sigma}) - n_{d\sigma}(1 - n_{d-\sigma})}{(w_{n_1} - \varepsilon_{d\sigma})(w_{n_4} - w_{n_1} + \varepsilon_{d\sigma} - \varepsilon_{d-\sigma})(w_{n_2} - \varepsilon_{d\sigma})} \\
& + \quad (-1)\, \delta_{w_{n_1}+w_{n_3}, w_{n_2}+w_{n_4}} (1/T) \quad \frac{1 - n_{d-\sigma}}{(w_{n_1} - \varepsilon_{d\sigma})(w_{n_2} - \varepsilon_{d\sigma})(w_{n_4} - \varepsilon_{d-\sigma})} \\
& + \quad \delta_{w_{n_1}+w_{n_3}, w_{n_2}+w_{n_4}} (1/T) \quad \frac{1 - n_{d\sigma}}{(w_{n_4} - \varepsilon_{d-\sigma})(w_{n_3} - \varepsilon_{d-\sigma})(w_{n_2} - \varepsilon_{d\sigma})} \\
& + \quad (-1)\, \delta_{w_{n_1}+w_{n_3}, w_{n_2}+w_{n_4}} \delta_{w_{n_2}, w_{n_3}} (1/2T^2) \quad \frac{n_{d\sigma}(1 - n_{d-\sigma}) - n_{d-\sigma}(1 - n_{d\sigma})}{(w_{n_1} - \varepsilon_{d\sigma})(w_{n_3} - \varepsilon_{d-\sigma})}
\end{aligned}
\tag{2.58}
$$

where for simplicity we use w_n instead of iw_n and where in the first term the factor $(1 - \delta_{w_{n_4}, w_{n_1}})$ excludes the possibility $w_{n_4} = w_{n_1}$ and as a result of the degeneracy of the singly occupied level such that $\varepsilon_{d\sigma} = \varepsilon_{d-\sigma}$. This possibility reappears in the last term and apart from this the above result could have been obtained from (2.44) by making the changes $w_n \to w$ and $2\pi\delta(\quad) \to \cdots$

$\ldots\ldots(1/T)\,\delta_{w_n,\ldots}$ in the limit $U \longrightarrow \infty$. In general, the temperature Green's functions in higher orders will have the same structure as the time temperature ones, apart from the effects described above associated with the 'particle-hole vertex' , the advantage of the latter being that they are much easier to calculate. It is easy to deduce in general that in this perturbation theory, the two pole structure of the Green's function will remain and it can be seen to be the result of the exclusion principle on the d-level being "correctly" treated .

The interesting self energy for finite T occurs as a result of the first term in (2.58)

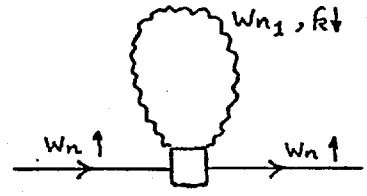


Fig.30

where $T_{ph}^{(T)} = \dfrac{1}{w_{n_1} - w_{n_4}}$ $\qquad (w_{n_1} \neq w_{n_4})$

The self energy contribution can be written:

$$\Sigma_d(w_n) = (-1)V^2T^2 \sum_k \sum_{n_1 \neq n} \frac{(n_{d\uparrow} - n_{d\downarrow})}{T(w_n - w_{n_1})(w_{n_1} - \varepsilon_k)} \qquad (2.59)$$

Of course to this order (2.59) simply vanishes because $n_{d\uparrow} = n_{d\downarrow}$ but it is instructive to evaluate (2.59) nevertheless.

The sum $\sum_{n_1}$ may be transformed into an integral which becomes

$$\frac{1}{2\pi i} \int_C \frac{f(\varepsilon)}{(w_n - \varepsilon)(\varepsilon - \varepsilon_k)}\, d\varepsilon \qquad (2.60)$$

where $f(\varepsilon) = \dfrac{1}{e^{\varepsilon/T} + 1}$ and the contour encircles the poles of $f(\varepsilon)$ which are at $\varepsilon = w_n = \dfrac{(2n+1)\pi T}{i}$ except the one at $\varepsilon = w_n$ (fig.31

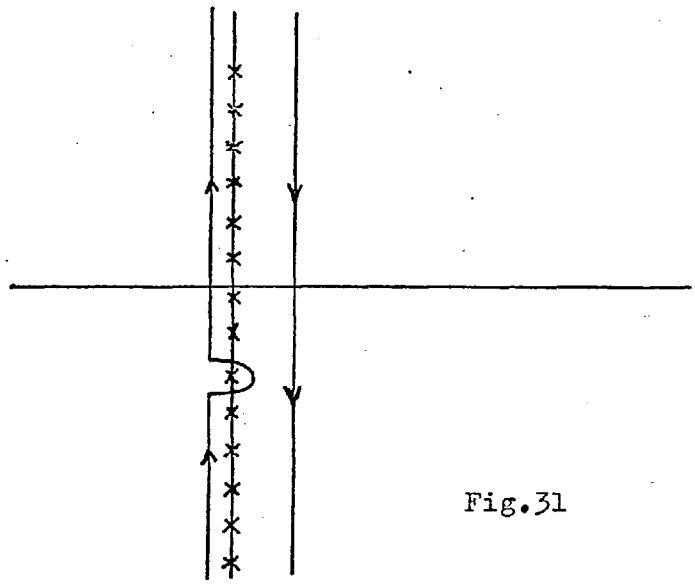


Fig.31

Closing the contour on the right hand side and left hand side by infinite semi circles , the contour C can be deformed into C which encloses the poles at $\varepsilon = \varepsilon_k$ and $\varepsilon = w_n$. The contribution due to the pole at $\varepsilon = \varepsilon_k$ to (2.60) is equal to

$$\sum_k \frac{f(\varepsilon_k)}{w_n - \varepsilon_k}$$

The double pole at $\varepsilon = w_n$ gives $\sum \frac{(-1/2)}{w_n - \varepsilon_k}$ together with a term which vanishes at T=0 . The contribution of interest to the self energy then becomes

$$\Sigma_d(w_n) = V^2 \sum_k \frac{(f(\varepsilon_k) - 1/2)(n_{d\uparrow} - n_{d\downarrow})}{w_n - \varepsilon_k} \qquad (2.61)$$

Apart from the factor $(n_{d\uparrow} - n_{d\downarrow})$, the above self energy can be identified as the Nagaoka-Abrikosov [6,22] type self energy obtained for the s-d model. It vanishes in this order but will remain inhigher orders. One could proceed to make partial summations, renormalizations, ...etc and obtain various approximate results for $G^T_{d\sigma}(w_n)$, but this is not the object of this section neither would it be particularly revealing in the present form. The object was to derive the self energies characteristic of the s-d model from a Green's function approach using the Anderson model, and to see what possible conclusions can be drawn

from such an approach in relation to the perturbation treatment in powers of U outlined in section A.

The perturbation treatment presented in this section cannot, unfortunately, in its present form supply an alternative to the method of section A. It is difficult to make it self-consistent. However it does provide some important support to the arguments presented at the end of the previous section. It suggests that a proper treatment of the exclusion principle on the d-level will maintain the 2-pole structure of the zero order Green's function as has been suggested by equation of motion analysis[40] and that this is also closely connected with the appearance of the zero energy transfer vertices which eventually are responsible for the Kondo anomalies (equa. 2.46). The non-cancellation of the 'unlinked' diagrams at finite temperatures is a serious disadvantag of this method, but on the other hand it provides a 'clue' as to what an alternative to the expansion of section A could be based on in the framework of the present theory. There is very good reason to believe that a large class of graphs including all the unlinked graphs of the numerator and denominator simply go to renormalize the bare distribution functions. As an example consider the derivation of the result (1.16)

$$G^T_{d\sigma}(w_n) = \frac{1 - \langle n_{d-\sigma} \rangle}{w_n - \varepsilon_{d\sigma}} + \frac{\langle n_{d-\sigma} \rangle}{w_n - \varepsilon_d - U}$$

from perturbation theory using a direct or non-Wick's theorem approach. In such an expansion, (2.4), it may be seen that from the numerator one has the following contributions to $G^T_d(\tau_1 - \tau_2)$

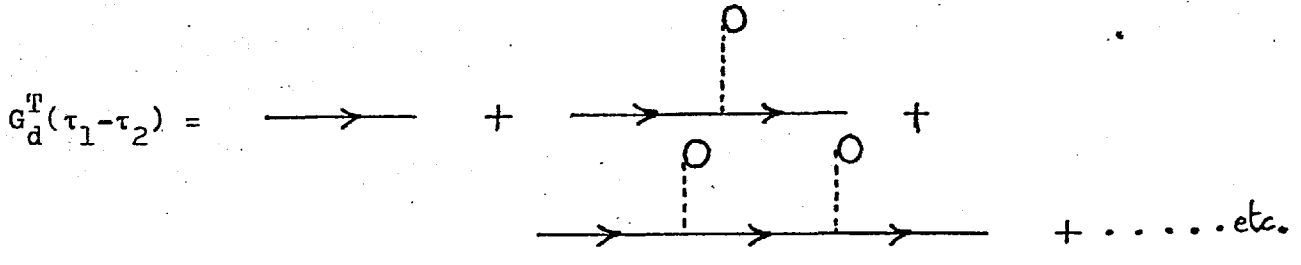


Fig. 32

together with unlinked graphs which may be represented

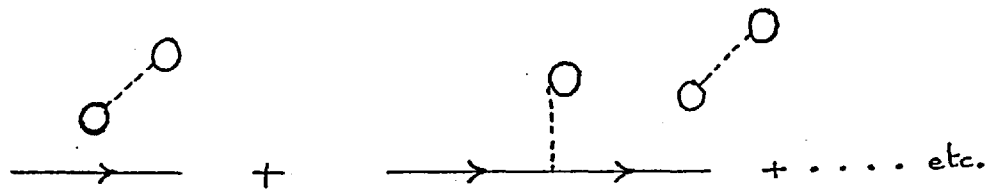


Fig.33

The propogator lines are taken as $(-1)\left[(1-n_{d\sigma})\theta(\tau_1-\tau_2) - n_{d\sigma}\theta(\tau_2-\tau_1)\right]\times e^{-i\varepsilon_{d\sigma}(\tau_1-\tau_2)}$ where the $n_{d\sigma}$ are operators as opposed to the Wick's theorem case where they represent zero order temperature averages, although the diagrams can be drawn in the same way. The contribution to the numerator of the expansion arising from the connected graphs may be written down immediately and gives

$$\frac{1 - f_{d-\sigma}}{w_n - \varepsilon_{d\sigma}} + \frac{f_{d-\sigma}}{w_n - \varepsilon_{d\sigma} - U} \qquad (2.62)$$

where $f_d = \dfrac{1}{e^{\beta\varepsilon_d} + 1}$

(2.62) already has the basic structure of (1.16). The contributions to the numerator from the unlinked graphs are

$$f_{d\sigma}f_{d-\sigma}\left[(-\beta)U + \frac{(-\beta)^2U^2}{2!} + \frac{(-\beta)^3U^3}{3!} + \ldots\text{etc}\right]\frac{1}{w_n - \varepsilon_{d\sigma} - U}$$

$$= \frac{f_{d\sigma}f_{d-\sigma}\,(e^{-\beta U}-1)}{w_n - \varepsilon_{d\sigma} - U}$$

Combining this with (2.62) and noting that the denominator $\langle S \rangle_o$ by definition is just $\dfrac{\mathrm{Tr}\, e^{-\beta H_d}}{\mathrm{Tr}\, e^{-\beta H_o}}$ we arrive back at (1.16).

This example goes to illustrate in a very typical way the above argument. Future work in this direction may be able to identify exactly graphs that renormalize the distribution functions and those that determine directly the analytic structure of the Green's function. In this way a self-consistent result along the line of those found by equations of motion techniques[12] may be obtained with the advantage that the physical processes included would be simply identifiable. Such an approach , it seems, will ultimately make it possible to bridge the gap between the spin fluctuation picture and the s-d picture in the description of the dynamical properties of the magnetic impurity system. The technique developed in the next Chapter overcomes many of the difficulties associated with an expansion in powers of the mixing interaction. It is a time independent method and gives a description of the physical parameters in the static limit.

CHAPTER III

TIME INDEPENDENT PERTURBATION THEORY FOR THE GRAND PARTITION FUNCTION Z AND THE FREE ENERGY F.

a) The transformation for Z

The time dependent approach, in particular to calculate the Green's function and the dynamic susceptibility was presented in the last Chapter. Section B was devoted to an investigation into the possibilities of a Green's function theory in which the expansion is carried out in powers of the mixing interaction and the Coulomb interaction is treated exactly. In this Chapter the same problem is tackled from another direction and a perturbation method is developed for the partition function Z and the Free energy F in which the Coulomb term is again treated exactly. From a knowledge of the Free energy it is possible to calculate the thermodynamic properties of the system e.g Entropy, static susceptibility,...etc. The Free energy F is related to Z according to the formula

$$F = -(\beta)^{-1} \log Z \tag{3.1}$$

where Z is given by

$$Z = \mathrm{Tr} \exp\left[(\mu N - H)\beta\right] \tag{3.2}$$

H is the Hamiltonian, $\beta = 1/kT$, and μ is the chemical potential determined from

$$\mu = \left(\frac{\delta F}{\delta N}\right)_{T,W} \tag{3.3}$$

and W is the volume.

If the Hamiltonian is split up into

$$H = H_o + H_I$$

where H_I is the perturbation, the expansion for Z then reads

$$\frac{Z(\mu,\beta)}{Z_o} = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_o^{\beta} d\tau_1 \ldots d\tau_n \left\langle T\left\{H_I(\tau_1) \ldots H_I(\tau_n)\right\}\right\rangle_o \tag{3.4}$$

where $\langle \; \rangle_o$ denotes the thermodynamic average over the unperturbed ensemble, Z_o is the partition function corresponding to H_o and $H_I(\tau)$ is given by

$$H_I(\tau) = e^{H_o\tau} H_I e^{-H_o\tau}$$

An alternative way of writing the expansion for $Z(\mu,\beta)$ is

$$Z(\mu,\beta) = \sum_{n=o}^{\infty} (-1)^n \int_{\beta>\tau_1>\tau_2\cdots\tau_n>0} d\tau_1 \, d\tau_2 \cdots\cdots d\tau_n \; Tr\left\{\exp(\mu N - H_o)\beta \; H_I(\tau_1)\ldots H_I(\tau_n)\right\} \tag{3.5}$$

Expansion (3.4) is more convenient when Wick's theorem applies for the unperturbed averages, in which case the time ordered averages may be expanded in terms of the usual connected and disconnected vacuum-vacuum graphs of field theory. The Free energy is then given by the sum of all the connected graphs.

For the Anderson Hamiltonian with

$$H_o = \sum_{\sigma} \varepsilon_{d\sigma} n_{d\sigma} + \sum_{k,\sigma} \varepsilon_{k\sigma} n_{k\sigma} + U n_{d\uparrow} n_{d\downarrow}$$

$$H_I = V \sum_{k,\sigma} (c^+_{d\sigma} c_{k\sigma} + c^+_{k\sigma} c_{d\sigma})$$

Wick's theorem cannot be used and it is easier to work with (3.5) in which the time integrals may be evaluated directly. This has been the approach used by Scalapino for the Anderson model[39], and Kondo for the s-d model[33]. It can be seen that the computational problem involved is so enormous that it is very tedious to obtain even the order V^4 result, let alone higher order contributions. The alternative method presented here removes this difficulty by transforming (3.5) into a time independent form using the technique developed by C.Bloch and C. de Dominicis [51]. These authors obtained a time independent expansion for the Free energy in terms of connected diagrams i.e when Wick's theorem applies, the technique they devised is however equally applicable to the problem of eliminating the time integrations

in the above expansion for $Z(\mu,\beta)$.

Thus following Bloch[52], we consider the function

$$< T\{H_I(\tau_1)H_I(\tau_2) \ldots\ldots\ldots H_I(\tau_n)\}> \qquad (3.6)$$

T means that the operators must be put in the same order as $\tau_1,\tau_2,\ldots\tau_n$ on the circle of time, Fig. 34.

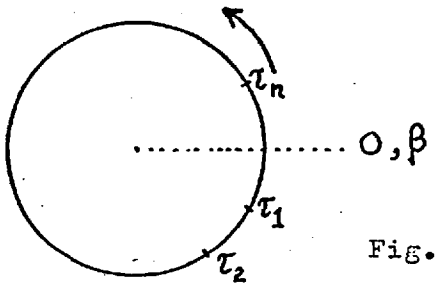


Fig.34

for this particular ordering i.e $\beta > \tau_1 > \tau_2 > \ldots\ldots\ldots \tau_n > 0$, (3.6) can be written

$$\frac{1}{Z_o} \quad Tr \left\{ \exp(\mu N\beta) \exp (\tau_1-\tau_n-\beta)H_o \quad H_I \exp (\tau_2-\tau_1)H_o \quad H_I \ldots\ldots H_I \right.$$

$$\left. \exp (\tau_n-\tau_{n-1})H_o \quad H_I \right\} \qquad (3.7)$$

This quantity depends only on the successive time differences and is invariant when all the times are rotated by the same angle on the circle of time. If some points cross the origin (0,β), it can be seen that the only change occuring in (3.7) is a circular permutation of the factors which leaves the trace unchanged.

The expression given for $Z(\mu,\beta)$ by (3.5) may be rewritten

$$\frac{Z(\mu,\beta)}{Z_o} = 1 + \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \int_D d\tau_1 \ldots\ldots d\tau_n \; <T\{H_I(\tau_1)\ldots H_I(\tau_n)\}>_0 \qquad (3.8)$$

where D is now the sum of the following domains of integration

$$D = \begin{cases} \beta > \tau_1 > \tau_2 > \ldots\ldots\ldots\ldots \tau_n > 0 \\ \beta > \tau_2 > \tau_3 > \ldots\ldots\ldots\ldots \tau_1 > 0 \\ \\ \\ \beta > \tau_n > \tau_1 \ldots\ldots\ldots\ldots \tau_{n-1} > 0 \end{cases}$$

The integrals corresponding to each of the individual domains of D in (3.8) are equivalent since they differ only by a permutation of the time variables and thus there is a factor 1/n outside the integrals. This kind of transformation is quite standard in the theory, it is for instance in a similar way that (3.4) can be obtained from (3.5).

The transformation of variables

$$\tau_1 = u_1 + \tau_n \qquad \tau_2 = u_2 + \tau_n \qquad \cdots \qquad \tau_{n-1} = u_{n-1} + \tau_n$$

changes the domain D into a new domain of integration given by

$$\beta > \tau_n > 0 \qquad\qquad \beta > u_1 > u_2 > \cdots\cdots\cdots u_{n-1} > 0$$

The τ_n integration in (3.8) may now be carried out immediately and we are left with

$$\frac{Z(\mu,\beta)}{Z_o} = 1 + \beta \sum_{p=1}^{\infty} \frac{(-1)^p}{p} \int_{\beta>u_1>u_2\cdots u_{p-1}>0} du_1 \cdots du_{p-1} \left\langle \left\{ H_I(u_1) \cdots H_I(u_{p-1}) H(0) \right\} \right\rangle \tag{3.9}$$

This expression can be further reduced by making the change of variables

$$v_1 = u_1 - u_2 \qquad v_2 = u_2 - u_3 \qquad \cdots\cdots \qquad v_{p-1} = u_{p-1}$$

which changes the domain of integration in (3.9) into

$$v_1 > 0 \ , \ v_2 > 0 \ , \ \cdots\cdots\cdots\cdots , v_{p-1} > 0$$

where $$v_1 + v_2 + \cdots\cdots\cdots v_{p-1} < \beta$$

The last restriction can be satisfied by multiplying the integrand with

$$\frac{1}{2\pi i} \int_{i\infty-a}^{-i\infty-a} \frac{d\varepsilon}{\varepsilon} \exp\left[\varepsilon(v_1 + v_2 + \cdots\cdots v_{p-1} - \beta)\right]$$

Clearly the integrations over $v_1, v_2, \cdots\cdots v_{p-1}$ may be carried out immediately and the final result is written

$$\frac{Z(\mu,\beta)}{Z_o} = 1 + (-\beta) \sum_{p=1}^{\infty} \frac{1}{2\pi i p} \int_{i\infty-a}^{i\infty-a} \frac{d\varepsilon}{\varepsilon} e^{-\beta\varepsilon} \left\langle H_I \left(\frac{1}{\varepsilon - \mathcal{L}} H_I \right)^{p-1} \right\rangle_o \tag{3.10}$$

The $\mathcal{E}$ correspond to the excitation energies, $\mathcal{E} = "H_o - E^o_{N,i}"$.
The contour in (3.10) can be closed by an infinite semi circle in the right hand plane (fig 35), so that it surrounds all the poles of the integrand (a can be chosen accordingly).

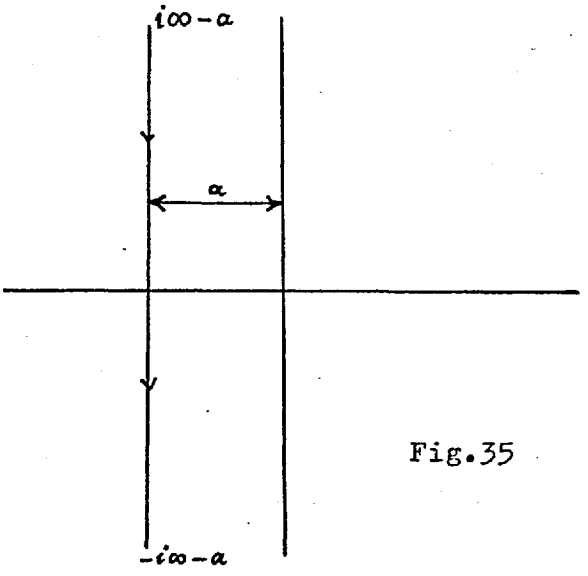


Fig.35

In this form, the expansion for $Z(\mu,\beta)$ is already considerably simpler for computational purposes than (3.5). It is similar to the result obtained by Bloch and de Dominicis for log Z except that in the latter only the connected graphs are to be summed over. The reason why the time independent transformation is valid for $Z(\mu,\beta)$ is because the only property that was needed to obtain it was the cyclic invariance of the trace in the integrand.

If H_o is written

$$H_o = H_B + H_d$$

where

$$H_d = \sum_{\sigma} \varepsilon_{d\sigma} n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow}$$

$$H_B = \sum_{k,\sigma} \varepsilon_{k\sigma} n_{k\sigma}$$

then $Z_o = Z_B Z_d$ and $Z_d = 1 + e^{-\beta\varepsilon_{d\sigma}} + e^{-\beta\varepsilon_{d-\sigma}} + e^{-\beta(2\varepsilon_d+U)}$

where all the energies are measured relative to the Fermi level μ.

The simplest way to evaluate the contributions in (3.10), is to represent

the quantity $Z_p(\varepsilon)$ by diagrams where $Z_p(\varepsilon)$ is defined as

$$Z_p(\varepsilon) = \left\langle H_I \left(\frac{1}{\varepsilon - \mathcal{E}} H_I \right)^{p-1} \right\rangle_0 \qquad (3.11)$$

The contributions to $Z_p(\varepsilon)$ may be represented by simple time ordered bubbles, where time increases clockwise and each bubble represents 'H_I' drawn in the order it appears in the trace going from right to left. Each bubble consists of an outgoing and ingoing line specifying an annihilation and creation operator respectively. Only graphs with an even number of bubbles contribute. To order V^2 for example there is a graph

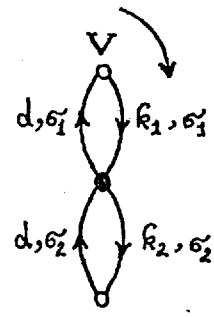


Fig.36

corresponding to $$V^2 \sum_{\sigma_1,\sigma_2} \sum_{k_1,k_2} \left\langle c^+_{d\sigma_2} c_{k_2\sigma_2} \frac{1}{\varepsilon - \mathcal{E}} c^+_{k_1\sigma_1} c_{d\sigma_1} \right\rangle_0 \qquad (3.12)$$

To be able to evaluate the excitation energies, we divide the graphs into 4 categories corresponding to the 4 possible eigenstates of H_d e.g (3.12) is rewritten

$$\frac{1}{Z_d} \sum_{\alpha} \sum_{k_i,\sigma_i} \left\langle \alpha \right| c^+_{d\sigma_2} c_{k_2\sigma_2} \frac{1}{\varepsilon - \mathcal{E}} c^+_{k_1\sigma_1} c_{d\sigma_1} \left| \alpha \right\rangle_B \; e^{-\beta\varepsilon_\alpha}$$

where α again refers to the impurity states with corresponding energy ε_α and the label B denotes that the thermodynamic average is to be taken for the band states only. The graphs may now be drawn to have in addition a label α specifying the state of the impurity over which the 'average'is to be evaluated and have a factor $n_{d\alpha}$ equal to $e^{-\beta(\varepsilon_{d\alpha})}/Z_d$, where

$$n_{\alpha_1} = n_{oo} = 1/Z_d \quad , \quad n_{\alpha_2} = n_{d\uparrow} = e^{-\beta(\varepsilon_{d\uparrow})}/Z_d$$

$$n_{\alpha_3} = n_{d\downarrow} = e^{-\beta(\varepsilon_{d\downarrow})}/Z_d \quad , \qquad n_{\alpha_4} = n_{dd} = e^{-\beta(2\varepsilon_d+U)}/Z_d \quad .$$

The excitation energies are then simply evaluated by keeping track of the occupation number of the d-level after each bubble. The thermodynamic averages over the band states are evaluated by Wick's theorem. The effect of the exclusion principle on the d-level will eliminate a great many possibilities and in general it is obvious there can be no more than 2 consecutive ingoing (or outgoing) d-lines of opposite spin (one of the same spin). Further restrictions are imposed of course according to the label of the particular graph.

As an example consider the following graph in order V^4 and contributing to α_1

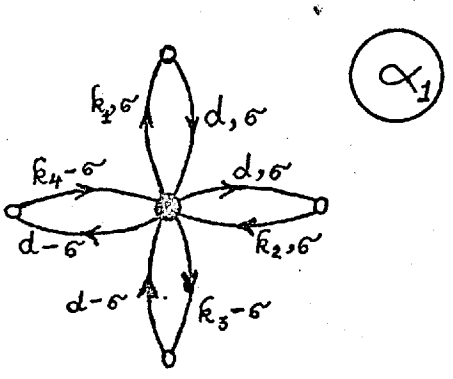


Fig.37

which gives

$$V^4\, n_{oo} \sum_{k_1,k_2,k_3,k_4} \frac{\langle c^+_{k_4-\sigma} c_{k_3-\sigma} c^+_{k_2\sigma} c_{k_1\sigma}\rangle_\alpha}{(\varepsilon - \varepsilon_{d\sigma} + \varepsilon_{k_1\sigma})(\varepsilon - \varepsilon_{k_2\sigma} + \varepsilon_{k_1\sigma})(\varepsilon - \varepsilon_{k_2\sigma} + \varepsilon_{k_1\sigma} - \varepsilon_{d-\sigma} + \varepsilon_{k_3-\sigma})}$$

$\langle\ \rangle_\alpha$ denotes that the thermodynamic average is to be taken over the band states and that the impurity state is "α", we shall be using this notation throughout. Thus we have

$$\langle c^+_{k_4-\sigma} c_{k_3-\sigma} c^+_{k_2\sigma} c_{k_1\sigma}\rangle_\alpha = (f_{k_3-\sigma}) \times (f_{k_1\sigma})\, \delta_{k_3k_4}\, \delta_{k_1k_2}$$

the contribution to $\frac{Z(\mu,\beta)}{Z_o}$ is obtained by multiplying by $\frac{e^{-\beta\varepsilon}}{\varepsilon n}(-\beta/2\pi i)n_\alpha$ and integrating over the contour C, which reduces to summing over the residues of the poles of $\frac{Z_{p,\alpha}(\varepsilon)e^{-\beta\varepsilon}}{\varepsilon\ p}(-\beta)\ n_\alpha$.

An alternative graphical representation may be used for the $Z_p(\varepsilon)$ which is sometimes more convenient. In this , the graphs are drawn in the usual way, i.e as if Wick's theorem applied in terms of connected and disconnected diagrams e.g

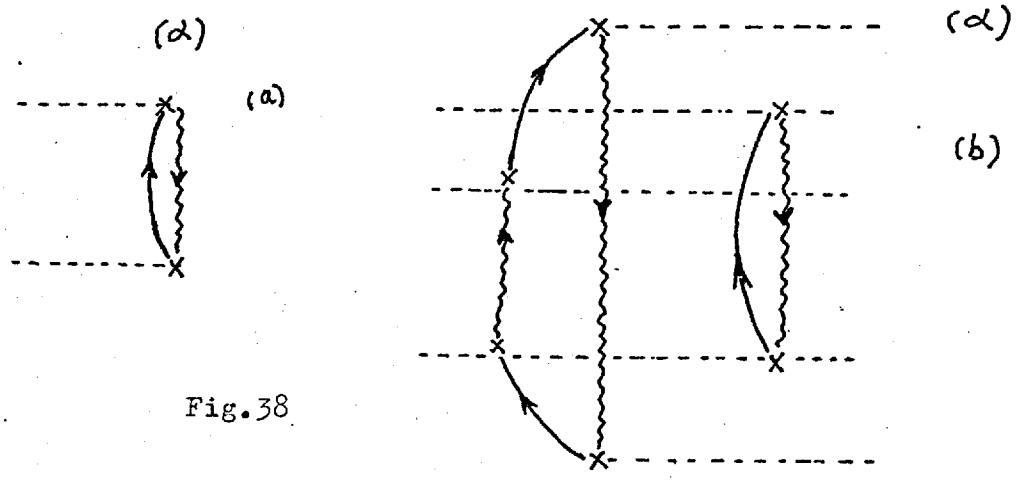


Fig.38

the wavy lines correspond to the $\underline{k}_\sigma$ lines and give rise to a factor $(1-f_{k\sigma})$ going up and $f_{k\sigma}$ going down. The occupation state of the impurity must here too be specified for each graph and thus for a graph corresponding to α , the d_σ-lines give a factor $(1-f_{d\sigma,\alpha})$ going up and $f_{d\sigma,\alpha}$ going down, where $f_{d\sigma,\alpha} = \langle\alpha|n_{d\sigma}|\alpha\rangle$ and is either 0 or 1. The complete contribution is then multiplied by n_α . The crosses denote the interaction times and give a factor V. The excitation energies are evaluated in the usual way where of course the occupation number of the d-state must be watched at each stage so that the Coulomb interaction is properly included. In this representation it is easy to see that there are two types of graphs , those overlapping in time and non overlapping ones . For example *(a,b)* fig. 38 is overlapping in time

whereas we could also have

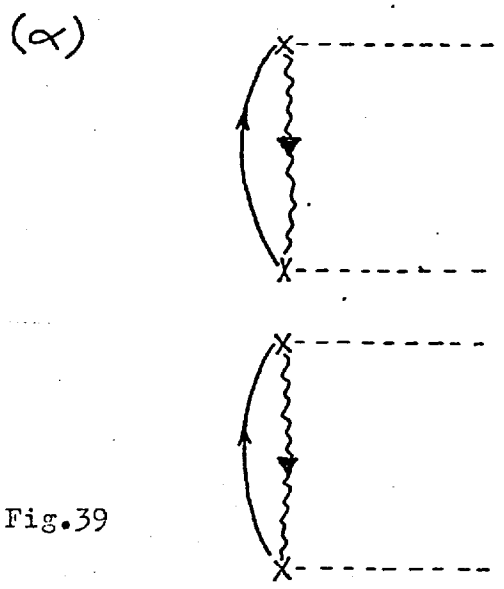


Fig.39

and it is obvious that all the possible graphs may be generated from the set of all overlapping graphs by simply repeating them in all possible non equivalent ways and where a non overlapping graph consisting of e.g 2, 3, ...n parts gives rise to an additional factor $1/\varepsilon$, $1/\varepsilon^2$, ... $1/\varepsilon^{n-1}$.

b) Elimination of the ε integration

In the expansion (3.10) for $Z(\mu,\beta)$, it turns out that the ε integration may in fact be completely eliminated which leads to an even greater reduction in the amount of work required to calculate the contributions. Consider in general the contribution to $Z_p(\varepsilon)/\varepsilon$ which may be written

$$\frac{Z_p(\varepsilon)}{\varepsilon} = \sum_{\alpha} n_\alpha \frac{1}{\varepsilon} \left\langle H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \cdots\cdots \frac{1}{\varepsilon - \mathcal{E}} H_I \right\rangle_\alpha \quad (3.13)$$

(3.13) gives rise to a set of non vanishing graphs each corresponding to one or at most two of the labels $\{\alpha\}$. Consider a graph contributing to α_i only, this has p bubbles and (p-1) excitation energies

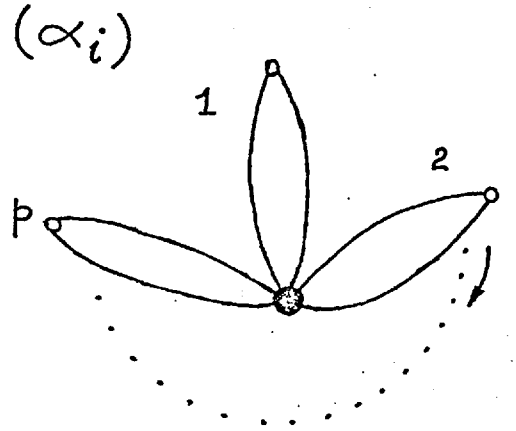


Fig.40

assume the excitation energies are labelled $\mathcal{E}_1, \mathcal{E}_2, \mathcal{E}_3, \ldots\ldots \mathcal{E}_{p-1}$. The contribution to Z/Z_o may be written

$$(-\beta/2\pi ip)\int_C d\varepsilon \frac{e}{\varepsilon}^{-\beta\varepsilon} \quad \frac{\langle A_1 A_2 \ldots\ldots\ldots\ldots A_p \rangle_{\alpha_i} n_{\alpha_i}}{(\varepsilon - \mathcal{E}_1)(\varepsilon - \mathcal{E}_2) \ldots\ldots\ldots (\varepsilon - \mathcal{E}_{p-1})} \qquad (3.14)$$

the A_p represent the operators occuring in the successive bubbles together with the appropriate momentum summations (the spins are taken to be fixed). Now consider the (p-1) other diagrams obtained from this one (fig 40) by rotation, each one is non vanishing in one of the states α and is therefore contained in the set of all (non vanishing) graphs to order p, by trace invariance. The contribution to Z/Z_o from the corresponding graph rotated by one bubble clockwise can be written

$$(-\beta/2\pi ip)\int_C d\varepsilon \frac{e}{\varepsilon}^{-\beta\varepsilon} \quad \frac{\langle A_2 A_3 \ldots\ldots\ldots\ldots A_p A_1 \rangle_{\alpha_j} n_{\alpha_j}}{(\varepsilon + \mathcal{E}_{p-1} - \mathcal{E}_1)(\varepsilon + \mathcal{E}_{p-1} - \mathcal{E}_2) \ldots\ldots\ldots (\varepsilon + \mathcal{E}_{p-1})} \qquad (3.15)$$

where the graph now contributes to the state α_j. When Wick's theorem is applied to the band states, the expression (3.14) corresponding to the original graph splits up into several terms each having a set of excitation energies, similarly for (3.15), the rotated graph. Then to each term from (3.14) there will correspond a term in (3.15) such

that the excitation energies are related as shown. The corresponding term is identified by assigning to the operators in (3.14) a fictitious time label and taking in (3.15) the term given by the contraction of the same time labelled pairs of operators. The corresponding α_j to α_i is obtained by noting that if (3.14) is non vanishing in a unique state α_i, then each successive rotation gives a non vanishing contribution to a unique α_j.

Assuming now that the expressions (3.14) and (3.15) refer to a pair of corresponding terms, then if all the excitation energies are different in (3.14), they will be different in the (p-1) corresponding terms coming from the set of (p-1) rotated graphs. It can be seen that the residue at $\varepsilon = 0$ in (3.15) gives the same result as the $\varepsilon=0$ residue in (3.14). The factor $e^{-\beta(\mathcal{E}_{p-1})}$ compensates for the difference in the Fermi factors arising out of the rotation of the band operators in the thermodynamic average, and the change $\alpha_i \longrightarrow \alpha_j$ in $e^{-\beta\varepsilon}\alpha_i$, It would be easy to show, with a convenient graphical representation that the complete contribution of corresponding terms are identical, from which one may immediately deduce that for the set of p corresponding terms in which all the (p-1) excitation energies are different only the $\varepsilon=0$ residue need be taken and the result multiplied by a factor p. This then gets rid of the $\frac{1}{p}$ in (3.14).

The general case when some of the excitation energies are equal, can be dealt with by noting that if θ of these energies are identical in (3.14), then the pole of order θ will appear θ times as the pole of $\varepsilon=0$ in the set of all rotated graphical contributions. Thus we need only take the residue at poles of $\varepsilon=0$ and multiply the result by $\frac{p}{\theta}$ where is the order of the pole at $\varepsilon=0$.

A general non-vanishing graph may contribute to either a single "α" or to two states $\{\alpha_i, \alpha_j\}$; in the latter case there

will also be two sets of excitation energies. When this graph is rotated it will contribute again to two possible states $\{\alpha'_i, \alpha'_j\}$. The rotated graph corresponding to α may be easily identified by noting that the first rotation can only change the occupation number of the d-level by one particle, similarly for the second rotation ...etc. The general result may now be written

$$\frac{Z(\mu,\beta)}{Z_o} = 1 + (-\beta)\sum_{p=1}^{\infty} \frac{1}{\theta} \mathrm{Res}_{\varepsilon=o}\left\{\frac{e^{-\beta\varepsilon}}{\varepsilon} Z_p(\varepsilon)\right\} \qquad (3.16)$$

where θ is the order of the pole at $\varepsilon = o$. This is merely an extension to this problem, and for Z, of the result obtained by Bloch and de Dominicis[52] for logZ when Wick's theorem applies. The proof is on similar lines, this extension was possible because the above result is again simply the consequence of the trace invariance and is independent of whether Wick's theorem applies or not except that in the former case the Free energy is given by the sum over the connected graphs only.

The simplest example of the above argument is provided in order V^2, consider for instance the graph

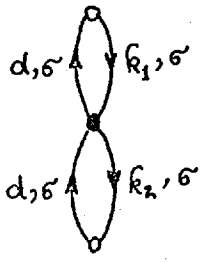


Fig.41

this graph contributes to both α_4 ($|d_\uparrow d_\downarrow\rangle$) and α_2 ($|d_\uparrow o\rangle$). The rotated graph also appears in the expansion e.g

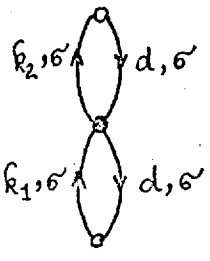


Fig.42

and contributes to α_1 ($|00\rangle$) and α_3 ($|d_\downarrow 0\rangle$). Clearly the 'equivalent' rotated graph for α_4 is the above graph for α_3. The contribution to Z/Z_o in the first case is

$$(-\beta/2\pi i)\sum_k \int_C \frac{e^{-\beta\varepsilon}}{2\varepsilon} \quad \frac{(1 - f_k)\ d\varepsilon}{\varepsilon - (\varepsilon_k - \varepsilon_d - U)} \quad \frac{e^{-\beta(2\varepsilon_d+U)}}{Z_d}$$

and in the second case

$$(-\beta/2\pi i)\sum_k \int_C \frac{e^{-\beta\varepsilon}}{2\varepsilon} \quad \frac{f_k \quad d\varepsilon}{\varepsilon - (\varepsilon_d + U - \varepsilon_k)} \quad \frac{e^{-\beta(\varepsilon_d\ )}}{Z_d}$$

clearly the total contribution of each of the above expressions is identical to the other. Similarly for α_1 α_2, and it is sufficient to consider the residue at $\varepsilon = 0$ in each contribution and drop the factor 1/2.

The expansion (3.16) represents a tremenduous simplification over (3.5). The contributions to every order can be evaluated without any difficulty and although the excitation energies cannot be deduced in the same automatic manner as for H_o non interacting, it turns out that the non-use of Wick's theorem leads to a considerable reduction in the number of terms by virtue of the restriction imposed by the exclusion principle for the impurity level. A trivial example of this is provided when

$$H_o = \sum_\sigma \varepsilon_{d\sigma} n_{d\sigma}$$

$$H_I = U\, n_{d\uparrow} n_{d\downarrow}$$

a direct evaluation of the right hand side of (3.16) leads to the series

$$\frac{(Z_d - Z_o)}{Z_o} = (-\beta)\langle n_{d\uparrow} n_{d\downarrow}\rangle_o \left[\mathrm{Res}_{\varepsilon=o} \left\{ e^{-\beta\varepsilon}(U/\varepsilon + U^2/2\varepsilon^2 + \ldots\ldots U^n/n\varepsilon^n \right\} \right]$$

which is easily evaluated and gives

$$\frac{Z_d - Z_o}{Z_o} = \frac{e^{-\beta(2\varepsilon_d+U)} - e^{-\beta(2\varepsilon_d)}}{Z_o}$$

which is the correct result. The Free energy is then obtained from (3.1) , if this result were to be obtained from the formula

$$F = F_o + \sum_{p=1}^{\infty} \frac{1}{\theta} \mathrm{Res}_{\varepsilon=o} \frac{e^{-\beta\varepsilon}}{\varepsilon} \left\langle H_I \left(\frac{1}{\varepsilon - \mathcal{L}} H_I \right)^{p-1} \right\rangle_{o,c} \qquad (3.17)$$

where c means that only the connected graphs are to be included, it is difficult to see how this could ever be achieved.

c) The limit $U \longrightarrow \infty$

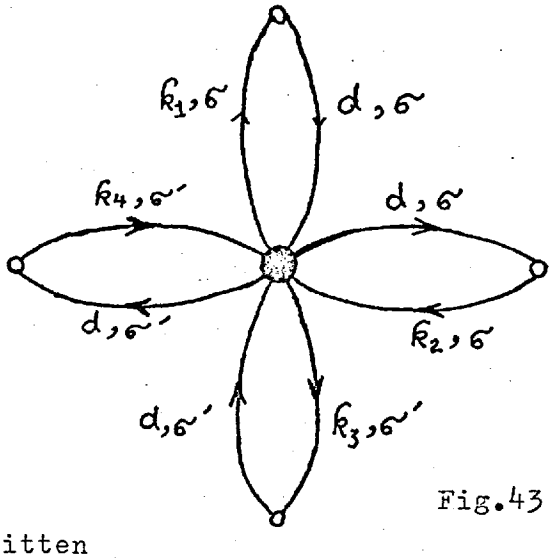
The limit $U \longrightarrow \infty$ leads to a great reduction in the number of graphs that have to be kept in each order. The state $|d_\uparrow d_\downarrow\rangle$ completely disappears in this limit and only the graphs refering to $\alpha_1, \alpha_2, \alpha_3$ need be considered. Furthermore, among these graphs only those give non vanishing contributions, where no two creation or annihilation operators of a d-state appear in consecutive bubbles anywhere in the graph.

d) Elimination of the non overlapping graphs

In the evaluation of $Z_p(\varepsilon)/\varepsilon$, where $Z_p(\varepsilon)$ is given by (3.11) , terms are encountered which lead to multiple poles at $\varepsilon = 0$. It was pointed out that in the usual representation these terms correspond to graphs which are non overlapping in time. In this section we shall devise a method of taking all these terms into account such that in the final analysis only the overlapping graphs need be evaluated, i.e contrbutions (of order 1) giving rise to simple poles

at $\varepsilon = 0$, and for which the result may be written down immediately using formula (3.16). This will then lead to a general formula for Z/Z_o .

Consider for instance the contribution to order V^4 corresponding to α_1 from the following diagram



(α_1)

Fig.43

which can be written

$$\sum_{k_1,k_3,\sigma} \frac{f_{k_3\sigma_2}\ f_{k_1\sigma}\ V^4\ n\alpha_1}{(\varepsilon + \varepsilon_{k_1\sigma} - \varepsilon_{d\sigma})(\varepsilon + \varepsilon_{k_3\sigma_2} - \varepsilon_{d\sigma_2})}\ \frac{1}{\varepsilon^2} \quad +$$

$$V^4 \sum_{k_1,k_3,\sigma} \frac{f_{k_1\sigma}(1 - f_{k_3\sigma})\ n\alpha_1}{\varepsilon(\varepsilon + \varepsilon_{k_1} - \varepsilon_{d\sigma})(\varepsilon_{k_1\sigma} - \varepsilon_{k_3\sigma} + \varepsilon)}$$

the additional $1/\varepsilon$ factor in the first term comes about because $\langle c_{k_1} c^+_{k_2} \rangle = (1 - f_{k_1})\ \delta_{k_1 k_2}$ and this term may be represented as

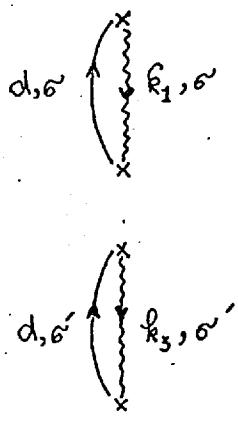


Fig.44

i.e as two non overlapping graphs. The second term of the above expression has a single pole at $\varepsilon=0$ when $k_1=k_3$ and therefore its contribution to Z/Z_o is just

$$(-\beta)V^4 \sum_{k_1,k_3,\sigma} \frac{f_{k_1\sigma}(1 - f_{k_3\sigma})\, n_{\alpha_1}}{(\varepsilon_{k_1\sigma} - \varepsilon_{d\sigma})^2(\varepsilon_{k_1\sigma} - \varepsilon_{k_3\sigma})}$$

When $k_1=k_3$, there is a double pole at $\varepsilon=0$ and the contribution must be evaluated according to (3.16). However there is an essential difference between the latter contribution and the first term of the expression which also exhibits a double pole at $\varepsilon=0$. In the last case it arises as a result of expanding the thermodynamic average, and essentially because of momentum conservation in H_o, it gives rise to a contribution to $Z(\mu,\beta)/Z_o$ of order

$$\frac{v^4}{N^2} \sum_{k_1,k_2} \longrightarrow O(1)$$

where $v/\sqrt{N} = V$. Whereas in the former case it occurs only when $k_1=k_3$ and gives a contribution of order

$$\frac{v^4}{N^2} \sum_{k} \longrightarrow O(1/N)$$

Thus in the limit $N \to \infty$ (or infinite volume) this contribution vanishes. Following Bloch[52], we shall call these vanishing excitation energies 'accidentally' vanishing, as opposed to the other case. In general the accidentally vanishing excitation energies lead to contributions of $O(1/N)$ and less to Z and F. Furthermore it is easy to see that the overlapping graphs give rise to simple poles at $\varepsilon=0$ to $O(1)$ and double and higher order poles to $O(1/N)$ and less. In the subsequent discussion we shall assume that in the case of interest, namely when the

number of particles is very large , these possibilities give rise to negligeable contributions to Z and therefore need not be considered. We shall come back to this point in Chapter IV.

Now let us consider in general $Z_{2p,\alpha}(\varepsilon)$ which is given by

$$Z_{2p,\alpha}(\varepsilon) = \langle H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \quad \ldots\ldots\ldots H_I \rangle_\alpha \tag{3.18}$$

the total number of ways $Z_{2p,\alpha}(\varepsilon)$ splits up into 2,3,.....p non overlapping parts (or parts disconnected in time) as a result of Wick's theorem applied to the band states, is simply enumerated. For instance in order V^4 there is only one way e.g giving

$$\langle\langle H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \rangle\rangle_\alpha \frac{1}{\varepsilon} \langle\langle H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \rangle\rangle_\alpha$$

hence in V^4 we write

$$\langle H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \rangle_\alpha = \langle\langle H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \rangle\rangle_\alpha$$

$$+ \quad \langle\langle H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \rangle\rangle_\alpha \frac{1}{\varepsilon} \langle\langle H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \rangle\rangle_\alpha$$

where the double bracket simply means that the possibility of a vanishing excitation energy to O(1) in the expansion of this term has been projected out e.g in view of the previous discussion we could write $\langle\langle \rangle\rangle_\alpha = \langle \rangle_{\mathcal{E} \neq 0, \alpha}$

In general it is easy to see that in the expansion of (3.16) in terms of overlapping contributions , the coefficient of the term constituted by the product of

s_1 parts of type x_1

s_2 ..... x_2

s_3 parts of type x_3

.....

s_m .....x_m

is just the coefficient of $(x_1)^{s_1}(x_2)^{s_2}\ldots\ldots(x_m)^{s_m}$ in the expansion of $(x_1 + x_2 + \ldots\ldots x_m + \ldots)^q$ where $q = (s_1 + s_2 + \ldots\ldots s_m)$, and is equal to

$$\frac{q!}{s_1!\, s_2! \ldots\ldots s_m!}$$

where

$$x_1 = \ll H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \gg_\alpha$$

$$x_2 = \ll H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \frac{1}{\varepsilon - \mathcal{E}} H_I \gg_\alpha$$

.....

$$x_n = \ll H_I \left(\frac{1}{\varepsilon - \mathcal{E}} H_I\right)^{2n-1} \gg_\alpha$$

The complete expansion for Z/Z_o may now be written

$$\frac{Z - Z_o}{Z_o} = (-\beta) \sum_{\alpha} \sum_{n=1}^{\infty} \frac{1}{n} \mathrm{Res}_{\varepsilon=o} \left\{ \frac{e^{-\beta\varepsilon}}{\varepsilon^n} \left[\sum_{p=1}^{\infty} \ll H_I \left(\frac{1}{\varepsilon - \mathcal{E}} H_I\right)^{p-1} \gg_\alpha \right]^n \right\}_{n_\alpha} \qquad (3.19)$$

where the factor 1/n comes about as a result of the pole of order n at $\varepsilon=o$. If we now define

$$g_\alpha(\varepsilon) = \sum_{p=1}^{\infty} \ll H_I \left(\frac{1}{\varepsilon - \mathcal{E}} H_I\right)^{p-1} \gg_\alpha \qquad (3.20)$$

then $g_\alpha(\varepsilon)$ corresponds to the sum of all possible overlapping graphs corresponding to α and the above result is not difficult to see, it merely says that the overlapping graphs may be repeated in all possible ways to generate all the graphs of $Z(\mu,\beta)$. If the double bracket is now taken to mean $< >_{\alpha, \mathcal{E}\neq 0}$, it must be emphasized that the above formula does not include the possibilities $\mathcal{E} = 0$ 'accidentally', on the

basis of the argument that they vanish in the limit of an infinite volume. Thus by definition $g_\alpha(\varepsilon)$ has no poles at $\varepsilon=0$ and the residue in the formula (3.19) may be evaluated according to the standard formula for a pole of order n due to $1/\varepsilon^n$ and we have

$$\frac{Z - Z_o}{Z_o} = (-\beta) \sum_{n=1}^{\infty} \sum_{\alpha} \frac{1}{n!} \frac{d}{d\varepsilon^{n-1}} \left[e^{-\beta\varepsilon} g_\alpha(\varepsilon)^n \right] \Bigg|_{\varepsilon=0} n_\alpha \qquad (3.21)$$

The result (3.21) may be viewed as a power series in β, the implication of which can be appreciated by considering the complete coefficient of $(-\beta)$ in (3.21). If we call this coefficient $\Delta E_\alpha \, n_\alpha$ then ΔE_α is given by

$$\Delta E_\alpha = \sum_{n=1}^{\infty} \frac{1}{n!} \frac{d}{d\varepsilon^{n-1}} \left[\left[g_\alpha(\varepsilon) \right]^n \right] \Bigg|_{\varepsilon=0} \qquad (3.22)$$

(3.22) may in fact be identified as the iterative solution of the self-consistency equation

$$\Delta E_\alpha = \sum_{p=1}^{\infty} \ll H_I \left(\frac{1}{\Delta E_\alpha - \mathcal{E}} H_I \right)^{p-1} \gg_\alpha \qquad (3.23)$$

about $\Delta E_\alpha = 0$. This is easy to check by iteration, and furthermore it can also be checked that the complete series (3.21) leads to the formula.

$$\frac{Z(\mu,\beta)}{Z_o} = \sum_{\alpha} \exp(-\beta \Delta E_\alpha) \, n_\alpha \qquad (3.24)$$

where ΔE_α is given by (3.23) perturbationally.

The above formulae are interesting and not totally unexpected because the zero temperature limit of ΔE_α can for example be identified to be the ground state energy shift expansion as given by Brillouin-

Wigner perturbation theory. This point is investigated further on.

The proof of (3.23) and (3.24) by series summation is very tedious, to obtain these results it is easier to proceed from another direction. Going back to (3.21) and rewriting it as

$$\frac{Z-Z_o}{Z_o} = \sum_{\alpha} \frac{(-\beta)}{2\pi i} \int_{C'} \frac{e^{-\beta\varepsilon}}{\varepsilon} \left[g_\alpha(\varepsilon) + \frac{g_\alpha^2(\varepsilon)}{2\varepsilon} + \ldots\ldots + \frac{g_\alpha^n(\varepsilon)}{n\varepsilon^{n-1}} \right] d\varepsilon \; n_\alpha \qquad (3.25)$$

where the contour C' now avoids all the poles of $g_\alpha(\varepsilon)$ and therefore also of $g_\alpha^2(\varepsilon)$ ...etc, and where none of the poles of $g_\alpha(\varepsilon)$ is by definition at $\varepsilon=o$. Equation (3.25) can also be written

$$\frac{Z-Z_o}{Z_o} = \sum_{\alpha} \left[\frac{(-1)}{2\pi i} \int_{C'} e^{-\beta\varepsilon} \left(\frac{g_\alpha(\varepsilon)}{\varepsilon^2} - \frac{g_\alpha'(\varepsilon)}{\varepsilon^1} \right) + \left(\frac{g_\alpha^2(\varepsilon)}{\varepsilon^3} - \frac{g_\alpha'(\varepsilon) g_\alpha(\varepsilon)}{\varepsilon^2} \right) + \right.$$

$$\left. \left(\frac{g_\alpha^3(\varepsilon)}{\varepsilon^4} - \frac{g_\alpha'(\varepsilon) g_\alpha^2(\varepsilon)}{\varepsilon^2} \right) + \ldots\ldots + \left(\frac{g_\alpha^n(\varepsilon)}{\varepsilon^{n+1}} - \frac{g_\alpha'(\varepsilon) g_\alpha^{n-1}(\varepsilon)}{\varepsilon^n} \right) d\varepsilon \right] n_\alpha \qquad (3.26)$$

where $g_\alpha'(\varepsilon) = \frac{d}{d\varepsilon}\left[g_\alpha(\varepsilon) \right]$ and the series in the square bracket in (3.26) is simply $(-1)\frac{d}{d\varepsilon}\left[G_\alpha(\varepsilon) \right]$, where $G_\alpha(\varepsilon)$ is the series in the first expression (3.25), the factor $(-\beta)$ outside having disappeared. The identity of (3.25) and (3.26) can be checked by evaluating the residue of the pole at $\varepsilon=o$ for the n'th term in each case e.g from (3.25) we have

$$\frac{(-\beta)}{n!} \frac{d}{d\varepsilon^{n-1}} \left(g_\alpha^n(\varepsilon)\, e^{-\beta\varepsilon} \right) \Bigg|_{\varepsilon=o}$$

and from (3.26) we obtain

$$\left[\frac{1}{n!} \frac{d}{d\varepsilon^{n-1}} \left\{ e^{-\beta\varepsilon} \left(n g_\alpha^{n-1}(\varepsilon) g_\alpha'(\varepsilon) + (-\beta) g_\alpha^n(\varepsilon) \right) \right\} - \frac{1}{(n-1)!} \frac{d}{d\varepsilon^{n-1}} \left(g_\alpha^{n-1}(\varepsilon) g_\alpha'(\varepsilon) e^{-\beta\varepsilon} \right) \right] \Bigg|_{\varepsilon=o} \qquad (3.27)$$

clearly the first and last term in (3.27) cancel and we are back to the previous expression. By definition $g_\alpha(\varepsilon)$ has no poles inside and on C' and from the point of view of perturbation theory we can sum the expression in (3.26) as a geometric series which yields

$$\frac{Z-Z_o}{Z_o} = \frac{n_\alpha}{2\pi i}\int_{C'} e^{-\beta\varepsilon}\left[\frac{g_\alpha(\varepsilon)}{\varepsilon(\varepsilon - g_\alpha(\varepsilon))} - \frac{g_\alpha'(\varepsilon)}{\varepsilon - g_\alpha(\varepsilon)}\right] d\varepsilon \qquad (3.28)$$

the pole at $\varepsilon=o$ in (3.28) contributes $(-1)\sum_\alpha n_\alpha$ which is just equal to (-1). The pole at $\varepsilon = g_\alpha(\varepsilon)$ which we assume with reference to the perturbation expansion (3.21) to be a simple pole and unique, contributes

$$\sum_\alpha n_\alpha \exp(-\beta\varepsilon_{c,\alpha})$$

where $\varepsilon_{c,\alpha}$ must be determined from

$$\varepsilon_{c,\alpha} = \sum_{p=1}^{\infty} \ll H_I\left(\frac{1}{\varepsilon_{c,\alpha} - \mathcal{E}} H_I\right)^{p-1} \gg_\alpha \qquad (3.29)$$

hence we have

$$\frac{Z}{Z_o} = \sum_\alpha n_\alpha \exp(-\beta\varepsilon_{c,\alpha})$$

clearly $\varepsilon_{c,\alpha} = \Delta E_\alpha$ and we obtain the result for Z, put forward in (3.24). It would appear that the above method leads to a more general result since it allows in principle more than one solution of the self-consistency equation $\varepsilon = g_\alpha(\varepsilon)$ to occur and thus to contribute to Z. Clearly the series representation of (3.28) can only give the iterative, or perturbational solution to this equation and is no longer valid if (3.29) has more than one solution. However this is not an unusual situation in perturbation theory and it will be seen that in this problem (Chapter IV), the correct viewpoint is obtained by looking at (3.29) or (3.23) as a self-consistency relation the correct solution

of which at T=0 is not necessarily the perturbational one , because of the Kondo effect when $\alpha = \{\alpha_2, \alpha_3\}$.

From (3.1) and (3.24) it follows that a knowledge of the ΔE_α's is sufficient to determine the Free energy, in practice however $\Delta\varepsilon_\alpha$ is calculated approximately and it is also desirable to have a direct perturbation expansion for F in powers of the mixing interaction so that the higher order terms can be analyzed in each order of the expansion for F.

e) Perturbation theory for F

To obtain the perturbation expansion of F, it is best to first go back to the time dependent formula for Z, and write for $\log(Z/Z_o)$ the well known expansion[53]

$$\log (Z/Z_o) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \int_o^\beta d\tau_1 \ldots\ldots d\tau_n \, M_n(\tau_1 \ldots\ldots \tau_n) \qquad (3.30)$$

where $M_1 = \langle H_I(\tau_1) \rangle_o$

$$M_2 = \langle T\{H_I(\tau_1)H_I(\tau_2)H_I(\tau_3)\rangle_o - \langle T\{H_I(\tau_1)\}\rangle_o \langle T\{H_I(\tau_2)\}\rangle_o$$

$$M_3 = \langle T\{H_I(\tau_1)H_I(\tau_2)H_I(\tau_3)\rangle_o - \langle T\{H_I(\tau_1)\}\rangle_o \langle T\{H_I(\tau_2)H_I(\tau_3)\}\rangle_o -$$
$$\langle T\{H_I(\tau_2)\}\rangle_o \langle T\{H_I(\tau_1)H_I(\tau_3)\}\rangle_o - \langle T\{H_I(\tau_3)\}\rangle_o \langle T\{H_I(\tau_1)H_I(\tau_2)\}\rangle_o$$
$$+ \quad 2\langle T\{H_I(\tau_1)\}\rangle_o \langle T\{H_I(\tau_2)\}\rangle_o \langle T\{H_I(\tau_3)\}\rangle_o$$

.....

T is the usual time ordering operator and the M_n's or time ordered semi-invariants are generated in the same way as the cumulants of Chapter II (2.32). The transformation of the M_n's into a time independent form is easily accomplished using the relation

$$\frac{(-1)^n}{n!}\int_0^\beta d\tau_1\, d\tau_2 \ldots d\tau_n \langle T\{H_I(\tau_1)H_I(\tau_2)\ldots\ldots H_I(\tau_n)\}\rangle_0 =$$

$$(-1)^n \int_{\beta>\tau_1>\tau_2\ldots\tau_n>0} d\tau_1\, d\tau_2 \ldots d\tau_n \langle H_I(\tau_1)H_I(\tau_2)\ldots\ldots H_I(\tau_n)\rangle =$$

$$\frac{(-\beta)}{2\pi i}\int_C d\varepsilon\, \frac{e^{-\beta\varepsilon}}{\varepsilon}\, \frac{1}{n} \langle H_I \left(\frac{1}{\varepsilon - \mathcal{L}} H_I\right)^{n-1}\rangle_0$$

and where each product in the expansion of the semi-invariants may be transformed separately. It is convenient to call

$$a_0 = 1$$

$$a_1 = 1!\,(-\beta/2\pi i)\int_C d\varepsilon\, \frac{e^{-\beta\varepsilon}}{\varepsilon} \langle H_I\rangle_0$$

$$a_2 = 2!\,(-\beta/2\pi i)\int_C d\varepsilon\, \frac{e^{-\beta\varepsilon}}{\varepsilon} \langle H_I \frac{1}{\varepsilon - \mathcal{L}} H_I\rangle_0$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$a_n = n!\,(-\beta/2\pi i)\int_C d\varepsilon\, \frac{e^{-\beta\varepsilon}}{\varepsilon} \langle H_I \left(\frac{1}{\varepsilon - \mathcal{L}} H_I\right)^{n-1}\rangle_0$$

If (3.30) is written as $\sum_{n=0}^{\infty} \frac{A_n}{n!}$ then it follows easily that the A_n's are given by

$$A_0 = 1$$

$$A_1 = a_1$$

$$A_2 = a_2 - a_1^2$$

$$A_3 = a_3 - 3a_2a_1 + 2a_1^3 \qquad \ldots\text{etc}$$

The A_n's are related to the a_n's in a similar way as the semi-invariants are related to the time ordered averages e.g the above relations can be obtained directly by assigning to the a's a fictitious 'time' label and expanding the quantities $\langle a^{(1)}a^{(2)}\ldots\ldots a^{(n)}\rangle_0$ in terms of

the A_n's, for example to third order we can write $a_1 = A_1$,
$a_2 = \langle a^{(1)} a^{(2)} \rangle_0 = A_2 + A_1^2$, $a_3 = \langle a^{(1)} a^{(2)} a^{(3)} \rangle_0 = A_3 + A_1^3 + 3A_1 A_2$
and similarly for higher orders. The advantage of writing things in this way is that one can obtain the expansion for $\log(Z/Z_0)$ directly in terms of the time independent quantities a_n.

To obtain a graphical representation for F, from which the contributions in each order can be evaluated, it is best to consider the relation (3.24)

$$\frac{Z}{Z_0} = \sum_\alpha n_\alpha \exp(-\beta \Delta E_\alpha)$$

and write it as a power series in β in the following way

$$\frac{Z}{Z_0} = \sum_\alpha n_\alpha \left[1 - \beta \Delta E_\alpha + \frac{(-\beta)^2 (\Delta E_\alpha)^2}{2!} + \ldots\ldots + \frac{(-\beta \Delta E_\alpha)^n}{n!} \ldots \right]$$

where the implicit dependence of ΔE_α and n_α on β is not considered. ΔE_α is given by the self-consistency relation (3.23) the expansion of which in powers of the mixing interaction can be represented by the series

$$\sum_{n=1}^{\infty} a^c_{\alpha,n} \eta^n \Big|_{\eta=1}$$

The $a^c_{\alpha,n}$ simply represent the complete contribution to order n of the perturbational solution of (3.23) and may be graphed in the same way as the contributions to Z i.e in terms of the 'time ordered' bubble graphs, except that each graph now in addition has a label 'c' to distinguish it from the previous ones. The contribution corresponding to each graph is evaluated in the same way as for Z except that the formula (3.19) now becomes

$$C \left\{ \sum_{p=1}^{\infty} \frac{1}{\theta} \mathrm{Res}_{\varepsilon=0} \left\{ \left\langle H_I \left(\frac{1}{\varepsilon - \mathcal{E}} H_I \right)^{p-1} \right\rangle_\alpha \frac{e^{-\beta\varepsilon}}{\varepsilon} \right\} \right\} \qquad (3.31)$$

where C means that only those contributions are to be included which are explicitly independent of β. The complete expansion for F can now be given and consists of the sum of all possible single (c,α) labelled graphs together with all possible combinations of disjoint (c,α) labelled graphs joined together by dashed lines in a simply connected way, where simply connected means that the complete graphs splits into two if cut at a dashed line.

e.g

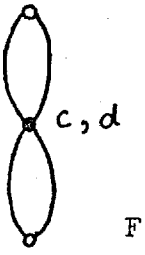


Fig.45

is a single (c,α) labelled graph of order V^2 and

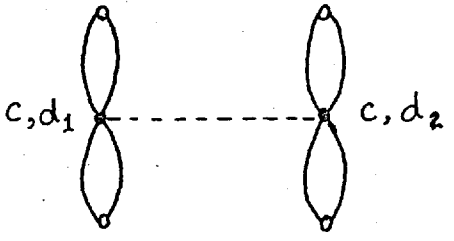


Fig.46

is a dashed line connected graph to order V^4. In addition we have the following rules: to a single graph labelled (c,α) there is a factor $M_1(\alpha)\ (-\beta)^0$. To a set of graphs labelled (c,α_{i_1}), (c,α_{i_2}), $\ldots\ldots(c,\alpha_{i_m})$ joined together by (m-1) dashed lines there corresponds a linking factor $M_m(\alpha_{i_1},\alpha_{i_2},\ldots\ldots,\alpha_{i_m})$ and a factor $\frac{(-\beta)^{m-1}}{m!}$. The α_i's as before refer to the 4 possible impurity states $(\alpha_1,\alpha_2,\alpha_3,\alpha_4)$. To evaluate the $M_n(\alpha_{i_1},\alpha_{i_2},\ldots\ldots,\alpha_{i_n})$, we associate the operators

$$
\begin{aligned}
(1 - n_{d\uparrow})(1 - n_{d\downarrow}) \quad &\text{to} \quad \alpha_1 \\
n_{d\uparrow}(1 - n_{d\downarrow}) \quad &\text{to} \quad \alpha_2 \\
n_{d\downarrow}(1 - n_{d\uparrow}) \quad &\text{to} \quad \alpha_3 \\
n_{d\uparrow} n_{d\downarrow} \quad &\text{to} \quad \alpha_4
\end{aligned}
\qquad (3.32)
$$

and calculate the $M_n(\alpha_{i_1}, \alpha_{i_2}, \ldots, \alpha_{i_n})$ in the same way as the A_n, and where the "α_i" are contained in the set of operators (3.32), e.g the first few M are calculated as follows

$$M_1(\alpha_i) = \langle \alpha_i \rangle_0 = n_{\alpha_i}$$

$$\langle \alpha_i \alpha_j \rangle_0 = M_2(\alpha_i, \alpha_j) + M_1(\alpha_i) M_1(\alpha_j)$$

$$\langle \alpha_i \alpha_j \alpha_k \rangle_0 = M_3(\alpha_i, \alpha_j, \alpha_k) + M_2(\alpha_i, \alpha_j) M_1(\alpha_k) + M_2(\alpha_i, \alpha_k) M_1(\alpha_j) + M_2(\alpha_k, \alpha_j) M_1(\alpha_i) + M_1(\alpha_i) M_1(\alpha_j) M_1(\alpha_k)$$

and $\langle \alpha_i \alpha_j \alpha_k \ldots \alpha_s \rangle_0 = \dfrac{\mathrm{Tr}\ e^{-\beta H_d} \{\alpha_i \alpha_j \alpha_k \ldots \alpha_s\}}{\mathrm{Tr}\ e^{-\beta H_d}}$, where "$\alpha_i$" = $n_{\alpha_i, op}$

To obtain the expansion for the M_n it is necessary to give the α separate labels even though some (or all) are necessarily identical. The order of the operators "α_i" in the linking factors is unimportant because they commute with each other.

The correct counting of the dashed line connected graphs is obtained by drawing them in a linear form, in which case non identical graphs are immediately identified , e.g

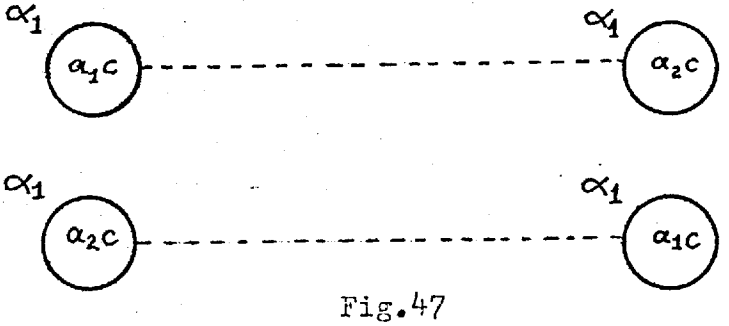


Fig.47

are non identical and must both be included to obtain F, even though

they both give the same contribution.

It is easy to see that the complete set of graphs consisting of : single, one dashed line , two dashed line , ..., connected graphs may be grouped together to give

$$F - F_o = \sum_{i=1}^{4} n_{\alpha_i} \Delta E_{\alpha_i} + (-\beta/2!) \sum_{i,j=1}^{4} (\Delta E_{\alpha_i})(\Delta E_{\alpha_j}) M_2(\alpha_i,\alpha_j) + \frac{(-\beta)^2}{3!} \sum_{i,j,k=1}^{4} (\Delta E_{\alpha_i})(\Delta E_{\alpha_j})(\Delta E_{\alpha_k}) M_3(\alpha_i,\alpha_j,\alpha_k) + \ldots \text{etc} \qquad (3.33)$$

This series can be identified to be the expansion in powers of η of

$$(-kT) \log \left\{ \left\langle \exp -\beta\eta \left(\sum_{i=1}^{4} \Delta E_{\alpha_i} n_{\alpha_i,op} \right) \right\rangle_o \right\} \qquad (3.34)$$

and where η is put equal to 1 at the end of the calculation. The $n_{\alpha_i,op}$ refer to the operators as defined by (3.32) , and the thermodynamic average is taken over H_d. Clearly (3.34) is identical to (3.1) with Z given by (3.24) when η is put equal to 1.

The equivalence of (3.33) with the expansion in powers of η of (3.34) follows by comparison with a general result given by Brout[53] for quantities of the form (3.34), it can also be obtained from (2.32) which gives the general defining relation for M_n in the limit when all the 'times ' go to zero and when the A_{α_i} are identified as the $n_{\alpha_i,op}$. When $(F - F_o)$ is written as in (3.33), it is obvious that any graphical representation of ΔE_α in powers of the interaction would be suitable to obtain a representation for F. The representation we used for ΔE_α , i.e the (c,α) labelled graphs, is not particularly elegant, it does however seem to be the most convenient when U is finite.

We shall now see that in the limit $U \longrightarrow \infty$, a representation may be used for ΔE_α, from which the contributions can be evaluated directly and one does not have to go through the procedure as for the bubble graphs. One may note that in the expansion (3.33) of $(F - F_o)$, all explicit dependence on β has been grouped together in a way which is very convenient when the limit $T \rightarrow 0$ is to be taken; this is carried out in Chapter IV.

f) Graphs for ΔE_α in the limit $U \longrightarrow \infty$.

It has already been mentioned that ΔE_α is given by the same kind of self-consistency relation as the ground state energy shift from Brillouin-Wigner perturbation theory, e.g we recall that

$$\Delta E_\alpha = \sum_{p=1}^{\infty} \ll H_I \left(\frac{1}{\varepsilon - \mathcal{G}} H_I \right)^{p-1} \gg_\alpha$$

The Rayleigh-Schrödinger expansion of ΔE_α will generate the same terms as occur in the ground state energy expansion, except that the summations are now extended over all the band states with weighting factors f_k and $(1-f_k)$ where $f_k = \dfrac{1}{e^{\beta(\varepsilon_k - \mu)} + 1}$ and μ is the chemical potential given by (3.3), whereas in the ground state energy expansion

$$f_k = 1 \qquad \varepsilon_k < \varepsilon_F$$

$$f_k = 0 \qquad \varepsilon_k > \varepsilon_F$$

where ε_F is the Fermi energy determined by the number of particles in the system, which is fixed. Thus the limit $T \longrightarrow 0$ of ΔE_α, except for the replacement $\mu \longrightarrow \varepsilon_F$, corresponds to the ground state energy shift $(E_{g,\alpha} - E_{o,\alpha})$ where $E_{o,\alpha}$ is the unperturbed ground state energy associated with the wave function $|\varphi_{o,\alpha}\rangle$ and

$$\varphi_{o,\alpha} = |\alpha\rangle \varphi_F$$

α denotes the impurity state and φ_F the unperturbed Fermi sphere. Clearly in this limit, the double bracket in (3.23) will play the same role as the projection operator P where P is given by

$$P = 1 - |\varphi_{o,\alpha}\rangle\langle\varphi_{o,\alpha}|$$

in the B.W perturbation formula. The difference between μ and ε_F is related to the fact that to obtain (3.23) we have been working with an unrestricted number of particles, whereas in the ground state energy formula , the number of particles is fixed. This question together with the limit $T \longrightarrow 0$ of F is dealt with in Chapter IV and has some interesting consequences. For the present purpose however, we merely want to show that a graphical representation for $\Delta E_{g,\alpha}$ can also be used for $\Delta E_{\alpha}(T)$ except that

$$\sum_{k<k_F} \longrightarrow f_k$$

$$\sum_{k>k_F} \longrightarrow (1 - f_k)$$

It is also well known that when Wick's theorem applies, the B.W formula reduces to the Goldstone expansion for the ground state energy (when the system is normal), given by

$$E_g - E_o = \sum_{p=1}^{\infty} \langle\varphi_o| H_I \left(\frac{1}{\mathcal{E}} H_I\right)^{p-1} |\varphi_o\rangle_c$$

where only the connected graphs in the usual representation are now included.

For the Anderson model in the limit $U \longrightarrow \infty$, we may use Wick's theorem with the effective interaction

$$H_I = V \sum_{k,\sigma} (1 - n_{d-\sigma}) \left[c^+_{d\sigma} c_{k\sigma} + c^+_{k\sigma} c_{d\sigma}\right] \qquad (3.35)$$

for the 3 possible unperturbed ground states: $|\alpha_1\rangle \varphi_F$; $|\alpha_2\rangle \varphi_F$, $|\alpha_3\rangle \varphi_F$.
The interaction (3.35) eliminates all contributions which go to zero in the limit $U \longrightarrow \infty$, and the average is taken over H_o which now simply is

$$H_o = \sum_{\sigma} \varepsilon_{d\sigma} n_{d\sigma} + \sum_{k,\sigma} \varepsilon_{k\sigma} n_{k\sigma} \qquad (3.36)$$

Thus in the limit $U \longrightarrow \infty$, the ΔE_α may be calculated perturbationally from the expansion

$$\Delta E_\alpha = \sum_{p=1}^{\infty} \left\langle H_I \left(\frac{1}{-\mathcal{E}} H_I \right)^{p-1} \right\rangle_{\alpha,c}$$

where H_I is given by (3.35) and the sum is over the connected graphs only, e.g

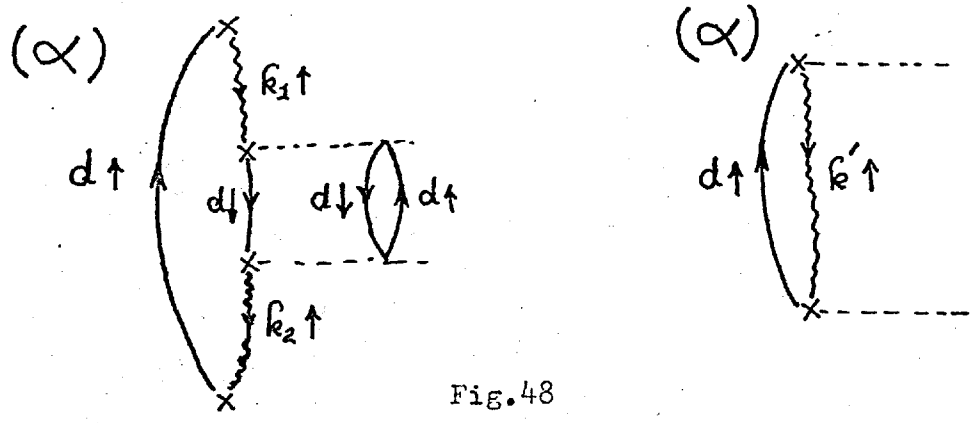


Fig.48

The excitation energies are evaluated in the usual way. To a k_σ-line going up there corresponds a factor $(1-f_{k\sigma})$, going down a factor $f_{k\sigma}$ where $f_{k\sigma} = \dfrac{1}{e^{\beta(\varepsilon_k - \mu)} + 1}$. To a d_σ-line going up there corresponds a factor $(1 - f^\alpha_{d\sigma})$, going down a factor $f^\alpha_{d\sigma}$. Where $f^\alpha_{d\sigma} = \langle \alpha | n_{d\sigma} | \alpha \rangle$.

It must be pointed out however, that Wick's theorem together with the effective interaction (3.35) can only be used when the average is taken over a specified d-state as in the above formulation. The thermodynamic Wick's theorem cannot be used because with H_o given

by (3.36), there is in the U infinity limit always an additional condititon $\langle n_{d\uparrow} n_{d\downarrow} \rangle = 0$.

This in the limit $U \longrightarrow \infty$, $(F - F_o)$ is given by the sum of connected and disconnected graphs of the type generated by the Goldstone expansion , and where the disconnected graphs are joined together by dashed lines with rules which follow immediately from the expansion of F as given by (3.33). Once the ΔE_α are known in every order, the contributions to $(F - F_o)$ can be written down almost immediately. The linking factors $M_n(\alpha_i , \alpha_i , \ldots . \alpha_{i_n})$ are calculated as before, for example

$$M_2(\alpha_1,\alpha_1) = \langle n_{\alpha_1} \rangle - \langle n_{\alpha_1} \rangle \langle n_{\alpha_1} \rangle$$
$$= n_{oo}(1 - n_{oo})$$

$$M_2(\alpha_1,\alpha_2) = 0 - \langle n_{\alpha_1} \rangle \langle n_{\alpha_2} \rangle$$
$$= - n_{d\uparrow} n_{oo}$$

The technique developed in this Chapter has many possibilities in relation to the impurity problem. In the next Chapter, we present some of the results which may be obtained with this method , perturbatio - nally and non perturbationally. Particular attention is paid to the static susceptibility and its behaviour in the limit $T \rightarrow 0$. We also make a brief analysis of the error associated with the neglect of the O(1/N) and smaller contributions.

CHAPTER IV

RESULTS AND DISCUSSION

a) Some perturbation theory results for F and the static susceptibility

The method developed in Chapter III will be used here to obtain some perturbational results for the Free energy and the static susceptibility.

The contributions to order V^2 to F come from the graphs

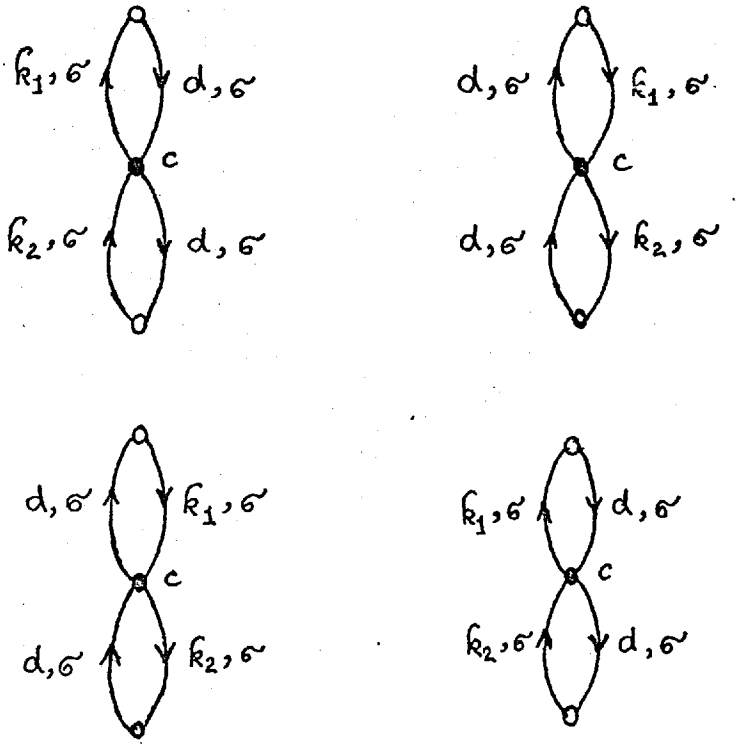


Fig.49

The result may be written down immediately and is :

$$V^2 \sum_{k,\sigma} \left[\frac{f_{k\sigma}\, n_{oo}}{\varepsilon_{k\sigma} - \varepsilon_{d\sigma}} + \frac{f_{k\sigma}\, n_{d-\sigma}}{\varepsilon_{k\sigma} - \varepsilon_{d\sigma} - U} + \frac{(1 - f_{k\sigma})\, n_{dd}}{\varepsilon_{d\sigma} - \varepsilon_{k\sigma} + U} + \frac{(1 - f_{k\sigma})\, n_{d\sigma}}{\varepsilon_{d\sigma} - \varepsilon_{k\sigma}} \right] \qquad (4.1)$$

In order V^4 , the 4 graphs :

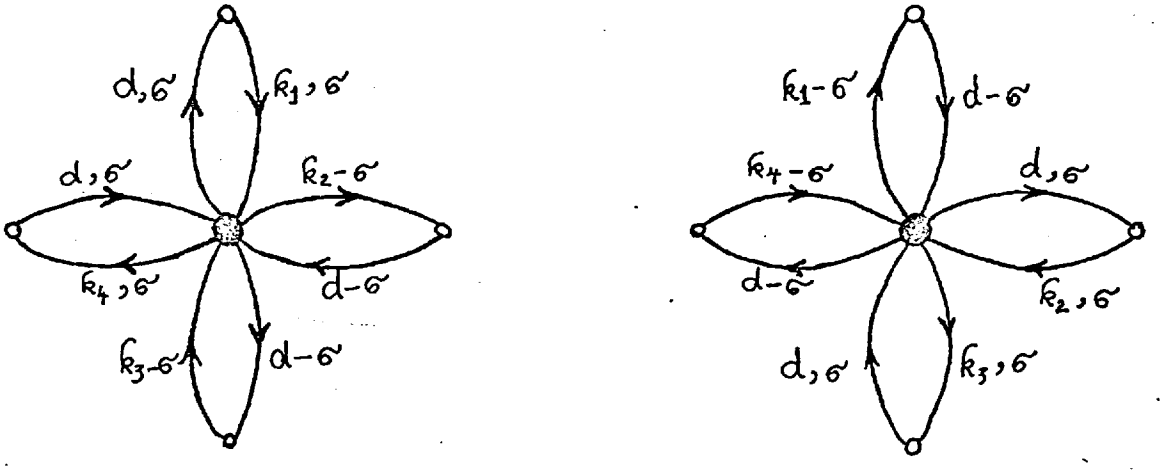
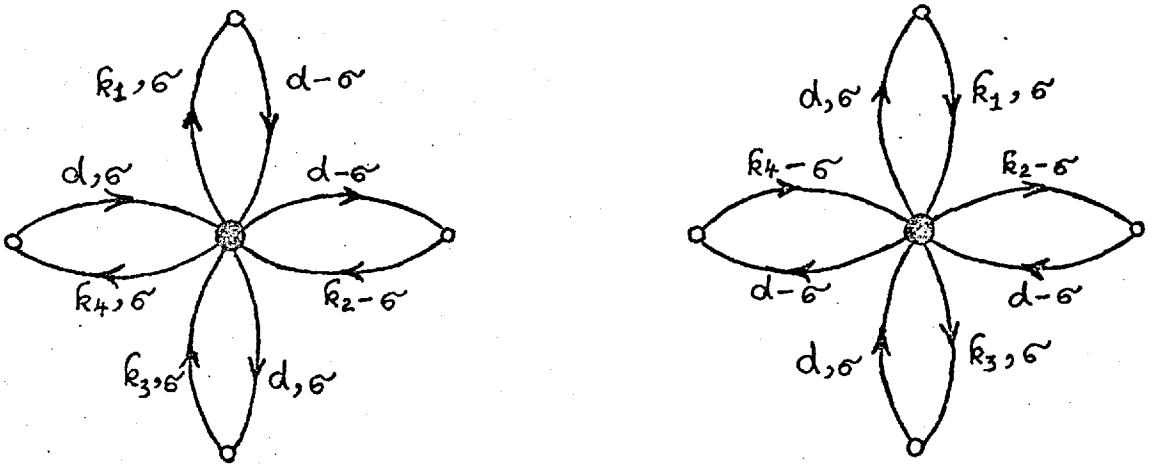


Fig.50



corresponding to $|d_\sigma, 0\rangle$ contribute :

$$V^4 \sum_{k_1, k_2, \sigma} \frac{f_{k_2-\sigma}(1 - f_{k_1\sigma})\, n_{d\sigma}}{(\varepsilon_{d\sigma} - \varepsilon_{k_1\sigma})^2(\varepsilon_{k_2-\sigma} - \varepsilon_{k_1\sigma} + \varepsilon_{d\sigma} - \varepsilon_{d-\sigma})}$$

$$V^4 \sum_{k_1, k_2, \sigma} \frac{f_{k_1-\sigma}(1 - f_{k_2\sigma})\, n_{d\sigma}}{(\varepsilon_{k_1-\sigma} - \varepsilon_{k_2\sigma} + \varepsilon_{d\sigma} - \varepsilon_{d-\sigma})(\varepsilon_{d\sigma} - \varepsilon_{k_2\sigma})(\varepsilon_{k_1-\sigma} - \varepsilon_{d_{-\sigma}} - U)}$$

$$V^4 \sum_{k_1, k_2, \sigma} \frac{f_{k_2-\sigma}(1 - f_{k_1\sigma})\, n_{d\sigma}}{(\varepsilon_{k_2-\sigma} - \varepsilon_{k_1\sigma} + \varepsilon_{d\sigma} - \varepsilon_{d-\sigma})(\varepsilon_{d\sigma} \doteq \varepsilon_{k_1\sigma})(\varepsilon_{k_2-\sigma} - \varepsilon_{d\sigma} - U)}$$

$$V^4 \sum_{k_1,k_2,\sigma} \frac{f_{k_1-\sigma}(1 - f_{k_2\sigma})\, n_{d\sigma}}{(\varepsilon_{k_1-\sigma} - \varepsilon_{k_2\sigma} + \varepsilon_{d\sigma} - \varepsilon_{d_{-\sigma}})(\varepsilon_{k_1-\sigma} - \varepsilon_{d-\sigma} - U)^2}$$

These 4 terms can be grouped together to give

$$V^4 \sum_{k_1,k_2,\sigma} \frac{f_{k_2-\sigma}(1 - f_{k_1\sigma})\, n_{d\sigma}}{(\varepsilon_{k_2-\sigma} - \varepsilon_{k_1\sigma} + \varepsilon_{d\sigma} - \varepsilon_{d-\sigma})} \left[\frac{1}{\varepsilon_d - \varepsilon_{k_1}} - \frac{1}{\varepsilon_d + U - \varepsilon_{k_2}}\right]^2 \qquad (4.2)$$

The order V^2 result together with the above contributions in V^4 correspond to the result obtained by Scalapino[39] by evaluating the time integrals directly.

The susceptibility is obtained by including in the zero order Hamiltonian a term corresponding to an external magnetic field h so that

$$H_o \longrightarrow H_o + \mu_B\, h\, S_{z,tot}$$

where μ_B is the Bohr magneton and $S_{z,tot}$ represents the "z" component of the total Spin operator. This term can be absorbed into H_o by redefining

$$\varepsilon_{k\uparrow,\downarrow} \longrightarrow \varepsilon_k \pm \mu_B\, h$$
$$\varepsilon_{d\uparrow,\downarrow} \longrightarrow \varepsilon_d \pm \mu_B\, h$$

The static susceptibility $\chi(T)$ is related to to the Free energy by

$$\chi(T) = -\left.\frac{\delta^2 F}{\delta h^2}\right|_{h=o} \qquad (4.3)$$

and the zero order susceptibility is calculated from F_o, where

$$(-\beta)\, F_o = \log\left(1 + e^{-\beta\varepsilon_d} + e^{-\beta\varepsilon_d} + e^{-\beta(2\varepsilon_d+U)}\right) \log Z_B^o \qquad (4.4)$$

(the label B refers to the Band states).

The region of interest physically, is $\varepsilon_d < 0$ and $2\varepsilon_d + U > 0$ (all the energies are measured relative to the Fermi level μ), this corresponds to the situation where the impurity is singly occupied by either an up or down spin at T=0. The low temperature susceptibility for the unperturbed system can be written

$$\chi^o(T) = - \left. \frac{\delta^2 F^o}{\delta h^2} \right|_{h=o} = \chi_p + \frac{\mu_B^2}{kT} \qquad (4.5)$$

χ_p is a temperature independent contribution from the conduction electrons, and μ_B^2/kT represents the Curie law for a free spin.

From (4.1), Scalapino evaluated the dominant contribution to the susceptibility and found in this order

$$\delta\chi^{(2)} = \frac{\mu_B^2}{kT} N(0)\, J \qquad (4.6)$$

where J is an antiferromagnetic s-d coupling in agreement with (1.38) and given by (1.39) in the region $\underline{k} = \underline{k}' \sim k_F$, and N(0) is the density of states at the fermi level . Scalapino evaluated the contribution due to (4.2) in the low temperature region and showed that it produces the logarithmic temperature dependence characteristic of the Kondo effect:

$$\delta\chi^{(4)} = \frac{\mu_B^2}{kT} N^2(0)\, J^2 \log(kT/W) \qquad (4.7)$$

where W is the band width and the density of states is taken to be constant. It is instructive to see how this logarithmic term arises. If in (4.2) we put

$$\left[\frac{1}{\varepsilon_d - \varepsilon_k} - \frac{1}{\varepsilon_d + U - \varepsilon_k} \right]^2 = J^2/4 \qquad (4.8)$$

then $$\delta\chi^{(4)}(T) = (J^2/4)\ -\frac{\delta^2}{\delta h^2}\left[\sum_{k_1,k_2,\sigma}\frac{f_{k_2-\sigma}(1-f_{k_1\sigma})\ n_{d\sigma}}{\varepsilon_{k_2}-\varepsilon_{k_1}}\right]\Bigg|_{h=0}$$

The (1/T) term comes from $$\frac{\delta}{\delta h}\left(n_{d\uparrow,\downarrow}\right)\Big|_{h=o} = \left(\mp\right)\frac{\mu_B}{2kT} \quad \text{(in low T)},$$

and the log(kT/W) term from

$$\frac{\delta}{\delta h}\left[\sum_{k_1,k_2}\frac{f_{k_{2\downarrow,\uparrow}}(1-f_{k_1\uparrow,\downarrow})}{\varepsilon_{k_2}-\varepsilon_{k_1}}\right]\Bigg|_{h=o} \qquad (4.9)$$

$f_{k\sigma}$ expanded about h=0 gives

$$f_{k\uparrow,\downarrow} = f_k\ (\mp)\ \mu_B\ h\ f_k(1-f_k)\ \beta \qquad + \ldots\ldots$$

and $\lim_{T\to 0}\ f_k(1-f_k)\ \beta = \delta(\varepsilon_k)$

So the dominant, or most divergent contribution in $T\to 0$ from (4.9) becomes

$$2\left(\mp\right)\mu_B\sum_k\frac{f_k}{\varepsilon_k} \qquad (\mp 2\mu_B)\int_{-\infty}^{\infty}\frac{N(\varepsilon)f(\varepsilon)}{\varepsilon}\,d\varepsilon \qquad (4.10)$$

for a constant density of states over a band of width $\left(\pm\right)W$ about the Fermi level, (4.10) becomes

$$\left(\mp\right)2\mu_B\ N(0)\ \log(kT/W)\ +\ \text{terms of lower order} \qquad (5)$$

The significance of (4.2) can be seen from the $U\to\infty$ graphical representation for ΔE_α given in Chapter III.

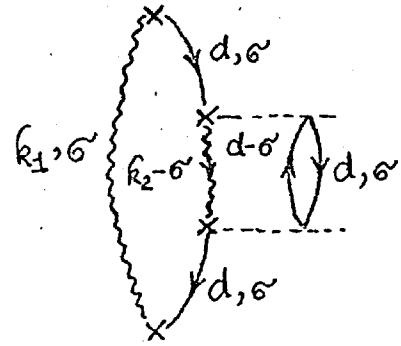


Fig.51

The above graph gives the $U \longrightarrow \infty$ limit of (4.2) and corresponds to a process in which the spin of the d-electron on the impurity is flipped in the intermediate state.

The remaining contributions to F in V^4 may be easily calculate in this technique. Since however one is primarily interested in the large U region, it is just as instructive to look at the U infinity limit. In this limit the remaining c labelled graphs correspond to

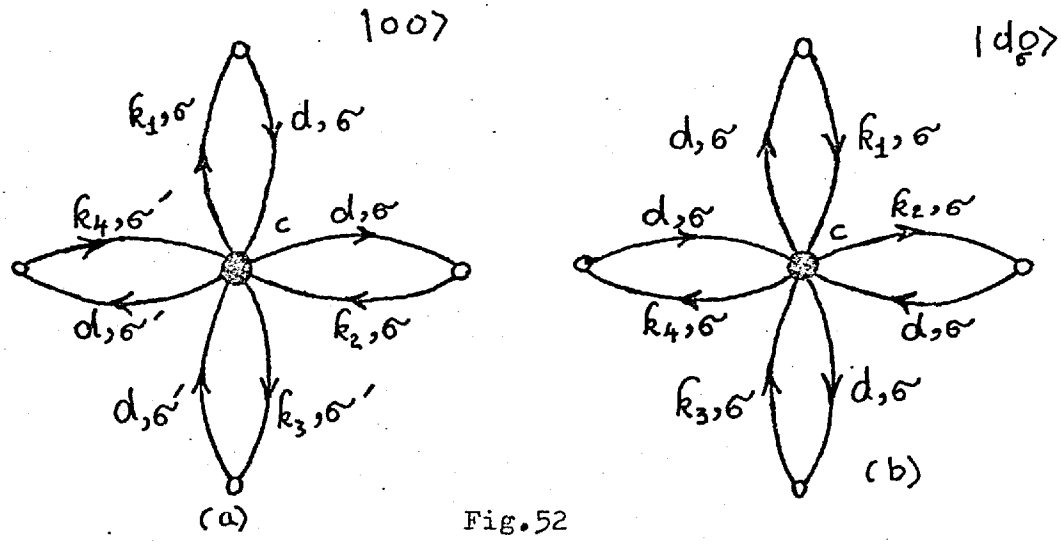


Fig.52

(a) giving

$$V^4 \sum_{k_1,k_2,\sigma} \frac{(1 - f_{k_2\sigma})(f_{k_1})\, n_{oo}}{(\varepsilon_{k_1} - \varepsilon_d)^2(\varepsilon_{k_1} - \varepsilon_{k_2})} +$$

$$(-1)V^4 \sum_{k_1,k_3,\sigma} \frac{f_{k_3\sigma}\ f_{k_1\sigma}\ n_{oo}}{(\varepsilon_{k_3} - \varepsilon_d)^2(\varepsilon_{k_1} - \varepsilon_d)}$$

and (b) giving

$$V^4 \sum_{k_1,k_2,\sigma} \frac{(1 - f_{k_1\sigma})f_{k_2\sigma}\ n_{d\sigma}}{(\varepsilon_d - \varepsilon_{k_1})^2(\varepsilon_{k_2} - \varepsilon_{k_1})} +$$

$$(-1)V^4 \sum_{k_1,k_3,\sigma} \frac{(1 - f_{k_3\sigma})(1 - f_{k_1\sigma})\, n_{d\sigma}}{(\varepsilon_d - \varepsilon_{k_3})^3(\varepsilon_d - \varepsilon_{k_1})}$$

together with the set of dashed line connected graphs :

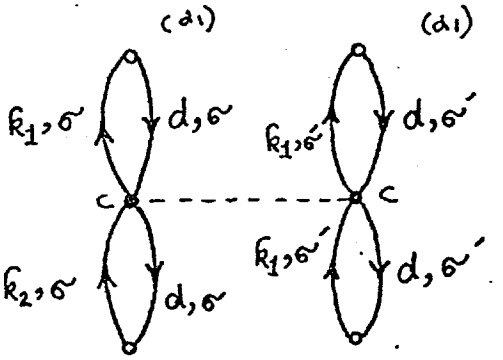


Fig.53

fig.53 contributes $M_2(\alpha_1,\alpha_1)\ (-\beta/2!)\ (a^c_{\alpha,2})^2 = (-\beta/2!)n_{oo}(1 - n_{oo})\ x$

$$V^4\left[\sum_{k,\sigma}\frac{f_{k\sigma}}{\varepsilon_k - \varepsilon_d}\right]^2$$

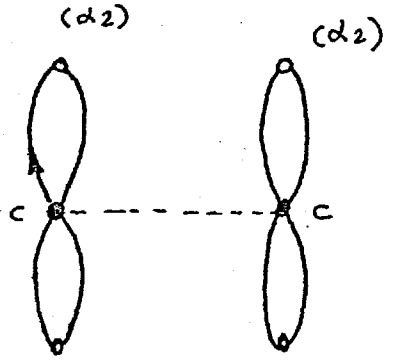


Fig.54

fig.54 gives $V^4(-\beta/2!)\ n_{d\uparrow}(1 - n_{d\uparrow})\left[\sum_{k}\frac{1 - f_{k\uparrow}}{\varepsilon_d - \varepsilon_{k\uparrow}}\right]^2$

similarly for $(\alpha_3)_2$----------$(\alpha_3)_2$ which gives

$$V^4(-\beta/2!)\ n_{d\downarrow}(1 - n_{d\downarrow})\left[\sum_{k}\frac{1 - f_{k\downarrow}}{\varepsilon_d - \varepsilon_{k\downarrow}}\right]^2$$

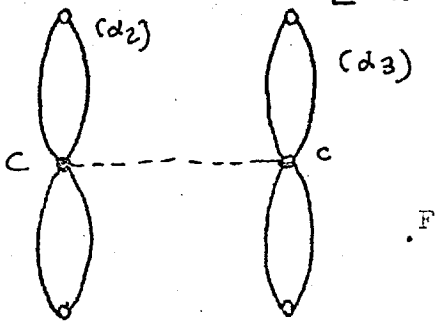


Fig.55

fig. 55 $\rightarrow (-\beta/2!)V^4(-n_{d\uparrow}n_{d\downarrow})\left(\sum_k \frac{1-f_{k\uparrow}}{\varepsilon_d-\varepsilon_{k\uparrow}}\right)\left(\sum_k \frac{1-f_{k\downarrow}}{\varepsilon_d-\varepsilon_{k\downarrow}}\right)$

similarly for $(\alpha_3)_2$----------$(\alpha_2)_2$

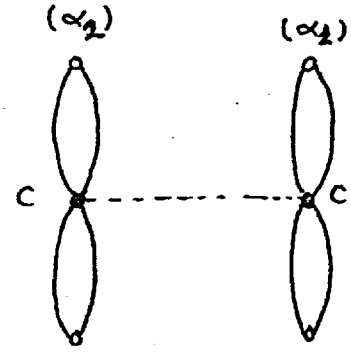


Fig.56

fig. 56 gives $(-\beta/2!)V^4(-n_{oo}n_{d\uparrow})\left(\sum_k \frac{1-f_{k\uparrow}}{\varepsilon_d-\varepsilon_{k\uparrow}}\right)\left(\sum_k \frac{f_k}{\varepsilon_k-\varepsilon_d}\right)$

similarly for $(\alpha_3)_2$----------$(\alpha_1)_2$

$(\alpha_1)_2$----------$(\alpha_2)_2$

(α_1)----------$(\alpha_3)_2$

An analysis of the graphs in fig. 52 shows that the dominant contribution in order V^4 is indeed due to (4.2), and that they give rise to contributions of $O(1/T)$ and less to $\chi(T)$; a similar result is obtained for the dashed line connected graphs in this order. Thus to order V^4 the result obtained for $\chi(T)$ including only the dominant terms in every order in the region $\varepsilon_d < 0$ and $2\varepsilon_d + U > 0$ and for low temperatures is given by

$$\chi(T) = \chi_p + \frac{\mu_B^2}{kT}\left[1 + N(0)J + N^2(0)J^2 \log(kT/W)\right] \qquad (4.11)$$

in agreement with the work of Scalapino[39], who further suggested that in higher orders the dominant contribution to $\chi(T)$ can probably

be written as a geometric series in powers of $N(0)J \log(kT/W)$, in which case the result for $\chi(T)$ including only the dominant term in every order would be

$$\chi(T) = \chi_p + \mu_B^2 \left[1 + \frac{N(0)J}{1 - N(0)J\log(kT/W)} \right] \qquad (4.12)$$

This result would imply that for J negative the perturbation treatment breaks down at temperatures below T_K, the characteristic or Kondo temperature given by (1.36), a conclusion very much expected on the basis of the Schrieffer-Wolff canonical transformation.

In this section, we shall show that the dominant contribution in each order of perturbation theory can indeed be represented in the form (4.12), and that there will also be lower order logarithmic terms in order V^n $n \geqslant 6$, in a similar way to the s-d model. For simplicity we shall be working in the U infinity limit which is sufficiently general for this purpose.

It turns out that in perturbation theory, the dominant contributions to $\chi(T)$ in the region of interest, come from the single c labelled graphs in other words those contained in

$$\delta F = \sum_{\alpha} n_\alpha \Delta E_\alpha \qquad (4.13)$$

and that the dashed line connected graphs make comparatively 'unimportant' contributions, except those connected by a single line. This is shown in section (b). Thus to order V^6 and in $U \longrightarrow \infty$, the dominant effects to $\chi(T)$ can be represented by the graph in fig.(57) which actually gives the complete contribution to $\left[n_{d\uparrow} \Delta E_\uparrow + n_{d\downarrow} \Delta E_\downarrow \right]$.

For $\sigma_1 = \sigma_2 = -\sigma$, the contribution is (fig. 57)

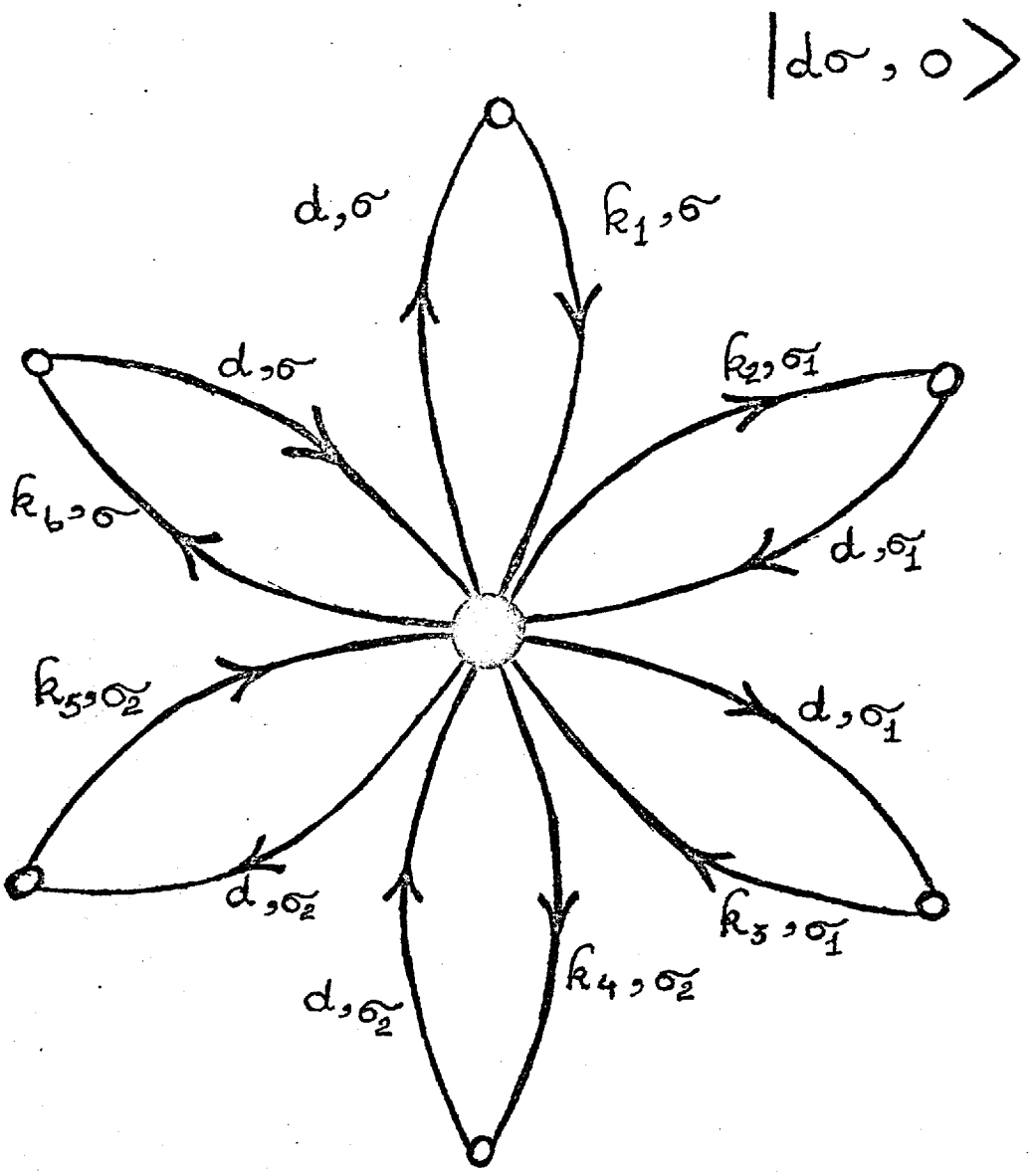

$|d\sigma, 0\rangle$
d,σ
k_1,σ
d,σ
k_2,σ_1
k_6,σ
d,σ_1
k_5,σ_2
d,σ_1
d,σ_2
k_3,σ_1
d,σ_2
k_4,σ_2

Fig.57

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})f_{k_2-\sigma}\,f_{k_3-\sigma}}{(\varepsilon_{d\sigma}-\varepsilon_{k_1\sigma})^3(\varepsilon_{k_2-\sigma}-\varepsilon_{k_1\sigma}+\varepsilon_{d\sigma}-\varepsilon_{d-\sigma})(\varepsilon_{k_3-\sigma}-\varepsilon_{k_1\sigma}+\varepsilon_{d\sigma}-\varepsilon_{d-\sigma})} \qquad (1)$$

$$+\ V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_2-\sigma})f_{k_3-\sigma}}{(\varepsilon_{d\sigma}-\varepsilon_{k_1\sigma})^2(\varepsilon_{k_3-\sigma}-\varepsilon_{k_1\sigma}+\varepsilon_{d\sigma}-\varepsilon_{d-\sigma})^2(\varepsilon_{d\sigma}+\varepsilon_{k_3-\sigma}-\varepsilon_{k_1\sigma}-\varepsilon_{k_2-\sigma})} \qquad (2)$$

For $\sigma_1 = \sigma$, $\sigma_2 = -\sigma$ and $\sigma_1 = -\sigma$, $\sigma_2 = \sigma$, the result is identical and the total contribution can be written

$$2V^6 \sum_{k_1,k_2,k_4,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(f_{k_4-\sigma})(f_{k_2\sigma})}{(\varepsilon_{d\sigma}-\varepsilon_{k_1\sigma})^3(\varepsilon_{k_2\sigma}-\varepsilon_{k_1\sigma})(\varepsilon_{k_4-\sigma}-\varepsilon_{k_1\sigma}+\varepsilon_{d\sigma}-\varepsilon_{d-\sigma})} \qquad (3)$$

$$(-2)V^6 \sum_{k_1,k_3,k_4,\sigma} \frac{n_{d\sigma}(1-f_{k_1\sigma})(1-f_{k_3\sigma})f_{k_4-\sigma}}{(\varepsilon_{d\sigma}-\varepsilon_{k_1\sigma})(\varepsilon_{d\sigma}-\varepsilon_{k_3\sigma})^3(\varepsilon_{d\sigma}-\varepsilon_{d-\sigma}+\varepsilon_{k_4-\sigma}-\varepsilon_{k_3\sigma})} \qquad (4)$$

$$(-1)V^6 \sum_{k_1,k_3,k_4,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_3\sigma})f_{k_4-\sigma}}{(\varepsilon_{d\sigma}-\varepsilon_{k_1\sigma})^2(\varepsilon_{d\sigma}-\varepsilon_{k_3\sigma})^2(\varepsilon_{k_4-\sigma}-\varepsilon_{k_3\sigma}+\varepsilon_{d\sigma}-\varepsilon_{d-\sigma})} \qquad (5)$$

$$(-1)V^6 \sum_{k_1,k_3,k_4,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_3\sigma})f_{k_4-\sigma}}{(\varepsilon_{d\sigma}-\varepsilon_{k_1\sigma})(\varepsilon_{d\sigma}-\varepsilon_{k_3\sigma})^2(\varepsilon_{k_4-\sigma}-\varepsilon_{k_3\sigma}+\varepsilon_{d\sigma}-\varepsilon_{d-\sigma})} \qquad (6)$$

The remaining contributions come from $\sigma_1 = \sigma_2 = \sigma$, this corresponds to the situation where there is no spin flip in the intermediate states and no logarithmic effects to $\chi(T)$ appear for such processes in any order. The contribution when $\sigma_1 = \sigma_2 = \sigma$ in order V^6 is given in the appendix (3).

It is not difficult to see that the dominant $\left[\log(kT/W)\right]^2 \frac{1}{T}$ contribution to $\chi(T)$ will come from the first and third term in the above results.

For $\sigma = \uparrow$, the first term can be rewritten:

$$(J/2)^3 \, n_{d\uparrow} \iiint \frac{d\varepsilon_1 \, d\varepsilon_2 \, d\varepsilon_3 \;\; N(\varepsilon_1)N(\varepsilon_2)N(\varepsilon_3)\left(1 - f(\varepsilon_{1\uparrow})\right)f(\varepsilon_{2\downarrow})f(\varepsilon_{3\downarrow})}{(\varepsilon_2 - \varepsilon_1)(\varepsilon_3 - \varepsilon_1)}$$

The $\left[\log(kT/W)\right]^2$ term comes from

$$\frac{\delta}{\delta h}\left\{\iiint \frac{d\varepsilon_1 \, d\varepsilon_2 \, d\varepsilon_3 \;\; N(\varepsilon_1)N(\varepsilon_2)N(\varepsilon_3)\left(-f(\varepsilon_{1\uparrow})f(\varepsilon_{2\downarrow})f(\varepsilon_{3\downarrow})\right)}{(\varepsilon_2 - \varepsilon_1)(\varepsilon_3 - \varepsilon_1)}\right\}\Bigg|_{h=0}$$

which leads to

$$2N^3(0)\,\mu_B\left[\log(kT/W)\right]^2$$

combining with $\frac{\mu_B}{kT}\frac{J^3}{8}$ and multiplying by 2 for both spin directions, we can write the dominant contribution to $\chi(T)$ due to this term

$$\frac{\mu_B^2}{2kT}\; N^3(0)\; J^3\left[\log(kT/W)\right]^2$$

A similar analysis of (3) leads to the same result as above, thus to this order the dominant contribution to $\chi(T)$ becomes

$$\frac{\mu_B^2}{kT}\; N^3(0)\; J^3\left[\log(kT/W)\right]^2$$

in agreement with the previous discussion.

Term (2) may be written

$$(J^3/8)\sum_{\sigma} n_{d\sigma} \iiint \frac{d\varepsilon_1 \, d\varepsilon_2 \, d\varepsilon_3 \; N(\varepsilon_1)N(\varepsilon_2)N(\varepsilon_3)\left(1 - f(\varepsilon_{1\sigma})\right)\left(1-f(\varepsilon_{2\sigma})\right)f(\varepsilon_{3\sigma})}{(\varepsilon_3 - \varepsilon_1)^2}$$

This term would appear to contain divergent contributions to $\chi(T)$, in the sense that the resulting integrals do not exist, however it must be combined (6) which shows a simialr behaviour. When this is done the result can be rewritten:

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\, f_{k_2-\sigma}(1 - f_{k_1\sigma})(1 - f_{k_3-\sigma})\,(-1)}{(\varepsilon_d - \varepsilon_{k_1})^2(\varepsilon_{k_2} - \varepsilon_{k_1})(\varepsilon_d - \varepsilon_{k_3})(\varepsilon_d - \varepsilon_{k_1} + \varepsilon_{k_2} - \varepsilon_{k_3})} +$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\, f_{k_2-\sigma}(1 - f_{k_1\sigma})}{(\varepsilon_d - \varepsilon_{k_1})^2(\varepsilon_{k_2} - \varepsilon_{k_1})^2} \left[\frac{f_{k_3\sigma}}{\varepsilon_d - \varepsilon_{k_3}} - \frac{f_{k_3-\sigma}}{\varepsilon_d - \varepsilon_{k_3}} \right]$$

The first term gives a $\frac{1}{T}\log(kT/W)$ contribution to $\chi(T)$, the second term vanishes for zero magnetic field but gives a similar contribution to $\chi(T)$. This is an example of a problem which often arises in perturbation theory. It shows that individual terms or diagrams may give rise to 'meaningless' contributions, but when grouped together in each order, the result converges. This point has been discussed by C. de Dominicis [54] in connection with the time independent technique. A similar argument applies for the present method where it should be noted that to obtain formula (3.16), one has implicitly grouped together 'p rotationally equivalent graphs ' and thus individual contributions need not be meaningful, and must be grouped together in each order.

In order V^8 for example, there will be individual terms contributing to F which behave as e.g

$$\int dx\ \frac{\varphi(x)}{x^3}$$

where $\varphi(x)$ does not $\longrightarrow 0$ as x^2 , however it has been be checked in

this order that when all such contributions are grouped together, the final result "converges."

It is not difficult to see that (4) and (5) give rise to contributions proportional to $J^3 \frac{\mu_B^2}{kT} \log(kT/W)$; writing (4) as

$$(J^2V^2/4) \left(\sum_{k_4,k_3} \frac{f_{k_4-\sigma}(1 - f_{k_3\sigma})\, n_{d\sigma}}{\varepsilon_{k_4} - \varepsilon_{k_3}} \right) \left(\sum_{k_1} \frac{1 - f_{k_1}}{\varepsilon_d - \varepsilon_{k_1}} \right)$$

and considering the $-\frac{\delta}{\delta h^2}$ of the first bracket, this simply gives the order V^4 dominant contribution in the same way as (4.2). The second bracket can be evaluated and is equal to $N(0) \log\left|\frac{\varepsilon_d}{W+\varepsilon_d}\right|$, thus the final result can be written

$$(V^2J^2)\, N^3(0) \log\left|\frac{\varepsilon_d}{W+\varepsilon_d}\right| \mu_B^2 \frac{\log(kT/W)}{T}$$

Similarly for (5) apart from the constant factors multiplying the temperature dependent part.

The dominant series for $\chi(T)$ to order V^6 can now be written

$$\chi(T) = \chi_p + \mu_B^2 \left[1 + N(0)J + N^2(0)J^2 \log(kT/W) + N^3(0)J^3 \left[\log(kT/W)\right]^2 \right] \qquad (4.14)$$

In addition there are lower order effects behaving as $\frac{1}{T} \log(kT/W)$ and $\frac{1}{T}$.

The graphical representation used to obtain the above results is not convenient for the purpose of generating the dominant terms to all orders. For this we shall now use the connected graphical representation in the U infinity limit discussed in Chapter III. The advantage of the bubble graphs over the connected graphs with H_I given by (3.35)

is that there are far fewer contributions to be considered in every order and therefore this representation is particularly useful when the complete result in a certain order is required. The reason for this is again related to the fact that in the connected graphical representation, Pauli's principle is not necessarily obeyed in each individual graph even though $f_{d\sigma} = 0$ or 1.

It was shown that in the limit $U \longrightarrow \infty$ and to order V^4, the key contribution to F comes from the graph

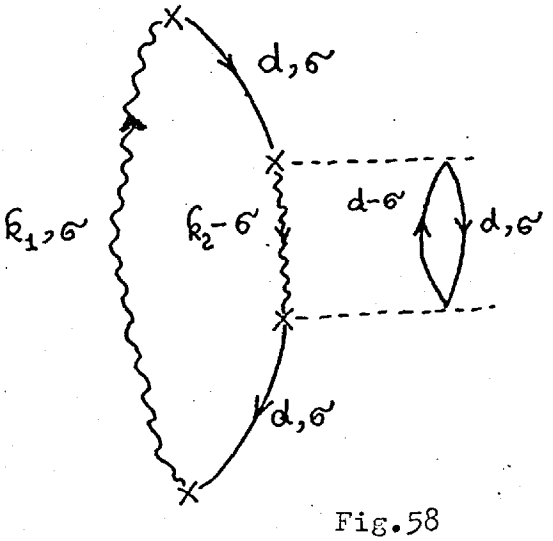


Fig.58

for V^6, the 3 graphs

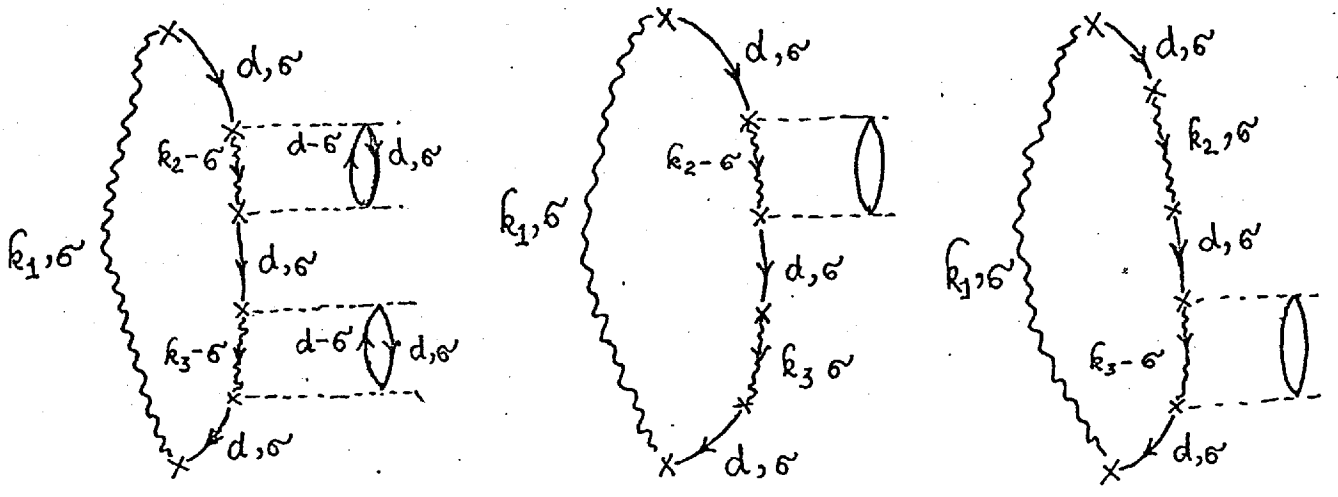


Fig.59

give the contributions (1) and (3) leading to the $\left[\log(kT/W)\right]^2$ term in $\chi(T)$. The first graph gives (1) andthe other two give equivalent contributions and lead to (3). The series leading to the dominant logarithmic terms in all orders for $\chi(T)$, can now be generated by repeating in all possible non equivalent ways the spin flip and direct self energies.

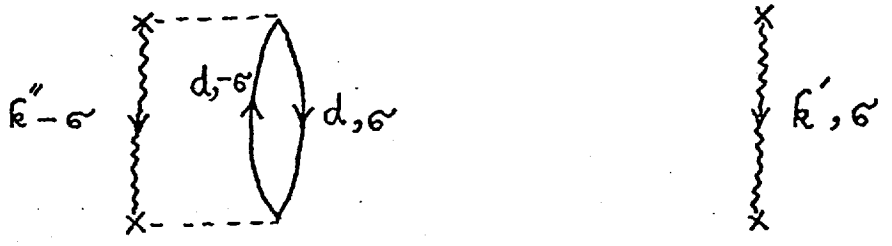


Fig.60

in the d_σ-line going down and closing the graph by a single k_σ-line going up .

The first term in the series is taken to be the graph of fig 58 and the result can be written

$$\delta F_D = \sum_{k_1,\sigma} n_{d\sigma} \left\{ \frac{\sum_{k_2,\sigma_2} \frac{V^4 (1 - f_{k_1\sigma}) f_{k_2\sigma_2}}{(\varepsilon_{d\sigma} - \varepsilon_{k_1\sigma})^2 (\varepsilon_{k_2\sigma_2} - \varepsilon_{k_1\sigma} + \varepsilon_{d\sigma} - \varepsilon_{d\sigma_2})}}{1 - \frac{V^2}{\varepsilon_{d\sigma} - \varepsilon_{k_1\sigma}} \sum_{k_3,\sigma_3} \frac{f_{k_3\sigma_3}}{\varepsilon_{k_3\sigma_3} - \varepsilon_{k_1\sigma} + \varepsilon_{d\sigma} - \varepsilon_{d\sigma_3}}} \right.$$

$$\left. - \frac{\sum_{k_2} \frac{(1 - f_{k_1\sigma}) f_{k_2\sigma} V^4}{(\varepsilon_{d\sigma} - \varepsilon_{k_1\sigma})^2 (\varepsilon_{k_2\sigma} - \varepsilon_{k_1\sigma})}}{1 - \frac{V^2}{\varepsilon_{d\sigma} - \varepsilon_{k_1\sigma}} \sum_{k_3} \frac{f_{k_3\sigma}}{\varepsilon_{k_3\sigma} - \varepsilon_{k_1\sigma}}} \right\} \qquad (4.15)$$

The first term in this expression includes graphs in which there are no spin flip self energies , i.e it includes the series : (Fig 61)

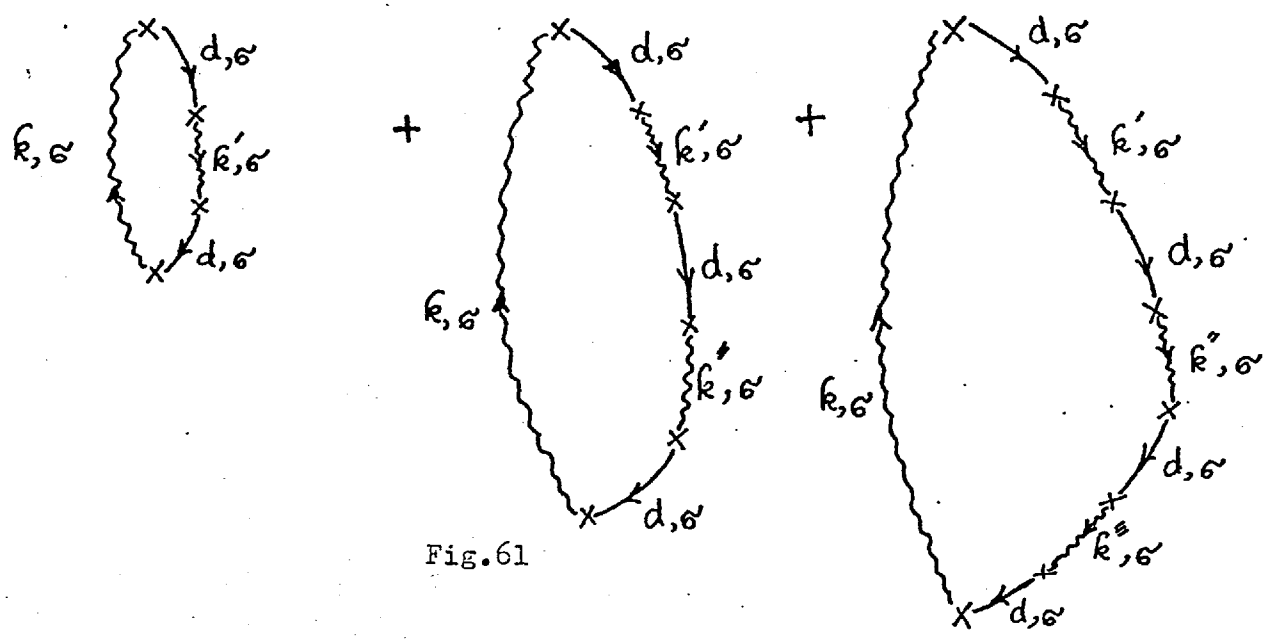


Fig.61

All these contributions are then exactly cancelled by the second term in (4.15) which corresponds precisely to the sum of the above series. On the other hand, these processes do not give rise to logarithmic terms in $\chi(T)$ when all the appropriate terms have been grouped together in every order. Thus we may neglect the second term in (4.15) and by making the usual approximation

$$\frac{V^2}{\varepsilon_d - \varepsilon_k} \approx J/2$$

δF_D becomes

$$\delta F_D = \sum_{k_1,\sigma} n_{d\sigma} \left\{ \frac{\frac{J}{4}^2 \sum_{k_2,\sigma_2} \frac{(1 - f_{k_1\sigma}) f_{k_2\sigma_2}}{\varepsilon_{k_2} - \varepsilon_{k_1}}}{1 - \frac{J}{2} \sum_{k_3,\sigma_3} \frac{f_{k_3\sigma_3}}{\varepsilon_{k_3} - \varepsilon_{k_1}}} \right\} \qquad (4.16)$$

writing

$$\delta F_D = \sum_{\sigma} n_{d\sigma}\, \delta F'_{D\sigma}$$

the dominant contribution to $\chi(T)$ comes from

$$\delta\chi_D(T) = -2 \sum_{\sigma} \frac{\delta n_{d\sigma}}{\delta h} \frac{\delta}{\delta h} (\delta F'_{D\sigma}) \Big|_{h=0}$$

and furthermore when $\frac{\delta}{\delta h}$ operates on $f_{k_1\sigma}$ inside the summation sign, then after some algebra the result becomes

$$\delta\chi_D(T) = \frac{\mu_B^2}{kT}\left[\frac{J^2N^2(0)\log(kT/W)}{1 - JN(0)\log(kT/W)}\right] \qquad (4.17)$$

which together with $\left[\frac{\mu_B^2}{kT} + \chi_p + \frac{N(0)J\mu_B^2}{kT}\right]$

then gives back (4.12). It is reasonable to expect that for finite U , J will simply be $\frac{2V^2}{U(\varepsilon_d+U)}$.

It would have been possible of course to make a more complete evaluation of $\chi(T)$ using the δF_D given by (4.16), however this series does not include sufficiently many graphs to yield anything more interesting than the dominant series. This result was expected on the basis of the analogy between the s-d model and the Anderson model and from the first few orders of perturbation theory. The technique developed here has made it possible to prove this and to show that the Kondo temperature T_K is indeed given by (1.36) which implies that perturbation theory breaks down for temperatures below T_K . For $T \gg T_K$ (4.12) predicts a Curie like behaviour for $\chi(T)$. As in the s-d model, the problem becomes focused on how to remove the divergence at $T=T_K$ in the physical parameters.

It was shown explicitly that in order V^6 there are logarithmic contributions to $\chi(T)$ of lower order than those summed in (4.17) and it is easy to see that this will be so in higher orders as well. These contributions are not negligeable in the low temperature region and a theory capable of going below T_K would at least have to include these terms partially[33] (e.g as in the Nagaoka-Hamann-Bloomfield theory)

In the framework of a perturbation theory for the static susceptibility, we have seen that the most divergent terms as $T \to 0$

come from the 'p' independent part of F, namely the right hand side of (4.13). In fact we may go further and write

$$\delta\chi(T) = -2\sum_{\sigma}\left(\frac{\delta}{\delta h} n_{d\sigma}\right)\left(\frac{\delta}{\delta h} \Delta E_{\sigma}\right)\Big|_{h=o} = \frac{\mu_B}{kT} \frac{\delta}{\delta h}\left(\Delta E_{\uparrow} - \Delta E_{\downarrow}\right)\Big|_{h=o} \qquad (4.18)$$

and the quantity of interest in perturbation theory is always $\frac{\delta}{\delta h}\left(\Delta E_{\sigma}\right)\Big|_{h=o}$ where $\Delta E_{\sigma}(h,T)$ is expanded in powers of the mixing interaction and we have taken $\Delta E_{\sigma} = \Delta E_{\alpha_2,\alpha_3}$. Assuming therefore that the inclusion of the lower order logarithmic terms in $\frac{\delta}{\delta h}\left(\Delta E_{\sigma}\right)\Big|_{h=o}$ will remove the divergence at $T = T_K$, (4.18) would probably still diverge in $T \longrightarrow 0$ because of the factor $1/T$. Such a behaviour is not in qualitative agreement with experiment, neither is it to be expected from general theoretical considerations (Cnapter 1). Thus to obtain a theory for $\chi(T)$ which is at least in qualitative agreement with experiment, two difficulties have to be overcome: the divergence at $T = T_K$ and in the limit $T \longrightarrow 0$. As far as the divergence at $T = T_K$ is concerned, the quantity of interest is $\Delta E_{\sigma}(h,T)$ and its derivative with respect to h, this can be calculated either using a direct perturbation expansion or 'non perturbationally' by seting up a self-consistency equation using (3.23). In the direct perturbation expansion it is difficult to renormalize the theory for finite U because one does not have a convenient graphical representation. On the other hand in $U \longrightarrow \infty$, one can use the connected graphical representation with H_I given by (3.35) with the help of which it is possible to renormalize in a self-consistent way those processes which lead to the logarithmic divergence

A direct way of seeing that the divergence at $T = T_K$ can be removed, is to consider $\Delta E_{\sigma}(h,T)$ which may be written

$$\underline{\Delta E}_\alpha(h,T) = \frac{\sum_{p=1}^{\infty} \mathrm{Tr}_\alpha \left\{ e^{-\beta(H_B+\mu_B h S_{z,B})} H_I \left(\frac{1}{\Delta E_\alpha(h,T) - \mathcal{E}} P H_I \right)^{p-1} \right\}}{\mathrm{Tr}\left\{ e^{-\beta(H_B+\mu_B h S_{z,B})} \right\}} \qquad (4.19)$$

where P is a projection operator which plays the same role as the double bracket, H_B is the Hamiltonian for the non interacting band electrons $S_{z,B}$ is the z component of the total spin operator refering to the band states only i.e

$$S_{z,B} = \sum_k (n_{k\uparrow} - n_{k\downarrow})$$

and α denotes that the d-average is to be taken in the state $|\alpha\rangle$. It follows that

$$\left.\frac{\delta\, \Delta E_\alpha(h,T)}{\delta h}\right|_{h=o} = \frac{\mu_B}{kT} \frac{\sum_{p=1}^{\infty} \ll S_{z,B} H_I \left(\frac{1}{\Delta E_\alpha - \mathcal{E}} H_I \right)^{p-1} \gg_\alpha}{1 - \left.\frac{\delta}{\delta\eta} g_\alpha(\eta)\right|_{\eta = \Delta E_\alpha}} \qquad (4.20)$$

$\Delta E_\alpha(T)$ is determined from

$$\Delta E_\alpha(T) = g_\alpha(\Delta E_\alpha(T))$$

and we have put $\left.\frac{\langle S_{z,B}\rangle}{kT}\right|_{h=o} = 0$. Note that the denominator of (4.20) cannot vanish because we have assumed that in (3.28) $\frac{1}{\varepsilon - g_\alpha(\varepsilon)}$ has a simple pole at $\varepsilon = \Delta E_\alpha$.

Using (4.20) and (3.23) it is possible in principle to obtain a self-consistent result for $\left.\frac{\delta}{\delta h}(\Delta E_\sigma)\right|_{h=o}$. In particular it can be seen that the excitation energies appearing in contributions

of the type $\sum \frac{f_k(1 - f_{k'})}{\varepsilon_k - \varepsilon_{k'}}$ ..... which eventually lead to the logarithmic divergences are now shifted to e.g $\sum \frac{f_k(1 - f_{k'})}{\Delta E_\alpha + \varepsilon_k - \varepsilon_{k'}}$ ..... which is no longer singular when k, k' approach the Fermi surface. However the situation is not quite so simple, for we shall see that the perturbation expansion of ΔE_σ is itself not valid in $T \to T_K$, and the problem has to be considered in greater detail.

b) Analysis of the dashed line connected graphs

The dashed line connected graphs to order V^4 were enumerated in section (a) and the dominant contribution to $\chi(T)$ was found to be of order $1/T$. In general the important contributions to $\chi(T)$ will come from graphs labelled (α_2, α_3) connected by dashed lines, where α_2 refers to $|d_\uparrow 0\rangle$ and α_3 to $|d_\downarrow 0\rangle$. There is of course a formula which exactly includes all the dashed line graphs in F, this is given by (3.34) and can be written

$$F - F_o = (-kT)\log\left\{\sum_\alpha n_\alpha \exp(-\beta \Delta E_\alpha)\right\} \qquad (4.21)$$

However this is essentially a 'non perturbational' result, and it is instructive to investigate the problem first from a perturbational viewpoint and then compare the result with a non perturbational approach.

From the series expansion for F given by (3.33) it follows that it is not actually necessary to analyze graphs in each order of V but for the present purpose it is sufficient to subdivide the contributions in terms of the number of dashed lines. The complete contribution to F consisting of two parts joined by one dashed line can be written

$$(-\beta/2) \sum_{i,j=1}^{4} M_2(\alpha_i, \alpha_j)\, \Delta E_{\alpha_i}\, \Delta E_{\alpha_j} \qquad (4.22)$$

The dominant contribution to $\chi(T)$ comes from

$$(-\beta/2)\left[M_2(\alpha_2,\alpha_2)\ \Delta E_{\alpha_2}\ \Delta E_{\alpha_3} + M_2(\alpha_3,\alpha_3)\ \Delta E_{\alpha_3}\ \Delta E_{\alpha_3} + 2M_2(\alpha_2,\alpha_3)\ \Delta E_{\alpha_2}\ \Delta E_{\alpha_3}\right] =$$

$$(-\beta/2)\left[n_{d_\uparrow}(1-n_{d_\uparrow})(\Delta E_\uparrow)^2 + n_{d_\downarrow}(1-n_{d_\downarrow})(\Delta E_\downarrow)^2 - 2n_{d_\uparrow}n_{d_\downarrow}(\Delta E_\uparrow)(\Delta E_\downarrow)\right] \qquad (4.23)$$

We note that for zero external magnetic field, (4.23) can be rewritten

$$(\Delta E_\sigma)^2\left[2n_d - 4n_d^2\right](-\beta/2)$$

this expression vanishes in the limit $T\to 0$ since $\lim_{T\to 0} n_d = 1/2$ when $\varepsilon_d < 0$, $2\varepsilon_d+U > 0$ and is zero otherwise. In fact the contribution to $\chi(T)$ due to (4.23) in the limit of low temperatures can be written

$$\delta\chi(T) = \frac{1}{kT}\left(\frac{\delta\ \Delta E_\sigma(h,T)}{\delta h}\right)^2\Bigg|_{h=o} \qquad (4.24)$$

where $\sigma = \uparrow$ or $\downarrow$.

It can be seen that the dominant contributions to $\chi(T)$ due to graphs joined together by a single dashed line will be of similar importance to the lower order logarithmic terms coming from (4.13). e.g $\frac{\mu_B^2}{kT}\left[\log(kT/W)\right]^s J^n$ $\quad s < n-1$

A detailed analysis of the 2,3,.... dashed line contributions to $\chi(T)$ has been carried out, and it has been found that they give rise to results which vanish in the limit $T\to 0$. The reason for this is not too difficult to see for we recall that by definition, the

2,3, ...n dashed line connected graphs have factors of $\beta^2, \beta^3, \ldots \beta^n$ and if their contributions to $\chi(T)$ were non vanishing in the limit as $T \rightarrow 0$, we should expect terms behaving as e.g $(1/T^2)\log(T)$, $(1/T^3)\log(T)$, ...etc. Such terms are clearly much more important in $T \rightarrow 0$ than the logarithmic ones considered previously and are not expected to occur in this problem neither have they been found in s-d model calculations. Hence it can be seen that when $\chi(T)$ is evaluated term by term from the series (3.33), then in the limit $T \rightarrow 0$ we need only consider the first two terms of this series. On the other hand this does not exclude the possibility that the sum of of the series gives a qualitatively different result to the term by term analysis. This in fact can turn out to be the case (see section 4).

To conclude briefly the work of the last section, we can now state that if $\chi(T)$ is to be calculated from a perturbation theory which is based on including the most important contributions to $\chi(T)$ in the limit $T \rightarrow 0$, then the result in the region $\varepsilon_d < 0$, $2\varepsilon_d + U > 0$ must be calculated from

$$\chi(T) = \chi_p + \frac{\mu_B^2}{kT} + \frac{\mu_B}{kT}\left[\left(\pm\right)^2 \frac{\delta}{\delta h}\Delta E_{\uparrow,\downarrow} + \frac{1}{\mu_B}\left(\frac{\delta}{\delta h}\Delta E_{\uparrow,\downarrow}\right)^2\right]_{h=0} \qquad (4.25)$$

where $\Delta E_\sigma(h,T)$ may be evaluated perturbationally using the various methods described previously.

Consider now the approximation for $\Delta E_\sigma(h,T)$ given by (4.16) and which leads to the dominant logarithmic series for $\chi(T)$. If to (4.16) we add the contribution to order V^2 we can then write

$$\left.\frac{\delta \Delta E_\sigma(h,T)}{\delta h}\right|_{h=0} = \frac{(J/2)\mu_B N(0)}{1 - N(0)J\log(kT/W)} \qquad (G = \uparrow) \qquad (4.26)$$

Substituting (4.26) in (4.25), $\chi(T)$ becomes

$$\chi(T) = \chi_p + \frac{\mu_B^2}{kT}\left[1 + \frac{N(0)J}{1 - N(0)J\log(kT/W)}\right] + \frac{\mu_B^2}{kT}\left[\frac{(J/2)N(0)}{1 - N(0)J\log(kT/W)}\right]^2 \qquad (4.27)$$

The last term in (4.27) is absent in (4.12) and is clearly of lower order in the logarithmic divergence when it is expanded in powers of J. In fact it corresponds to the dominant contribution of the graphs connected by a single dashed line. The interesting feature of this term is the fact that it is actually more divergent than the so called dominant series when $T \to T_K$. This example clearly shows that in low temperatures, the lower order logarithmic terms are not negligeable.

$\chi(T)$ as given by (4.25) will not be meaningful in $T \to T_K$ unless $\Delta E_\sigma(h,T)$ is suffieciently well approximated so that the divergence at $T = T_K$ is removed. Assuming that when the lower order logarithmic terms are included (or at least partially) (4.25) is defined in $T \lesssim T_K$ to obtain a qualitatively correct result for $\chi(T)$ would require that the

$$\lim_{T \to 0} \frac{1}{kT}\left[\mu_B \pm \frac{\delta \Delta E_{\uparrow,\downarrow}(h,T)}{\delta h}\right]^2$$ is finite. The

significance of this condition is investigated further in (d) where it is obtained in a more general context.

In the next two sections we look at the susceptibility and the Free energy from a 'non perturbational angle ' by using the equations (3.23) and (4.21) . Particular attention is paid to the limit $T \to 0$ for F and $\chi(T)$. The low temperature limit for $\chi(T)$ is particularly important in view of the incapacity of present day theories to describe it. It appears that the result obtained for F in Chapter III may be able to throw some light on the question of

the exact cancellation of the local moment in the s-d region.

c) The limit $T \rightarrow 0$ for the Free energy

The perturbation expansion for F is obtained from (3.33) and by using the Rayleigh-Schrödinger or iterative expansion of the self-consistency relation (3.23) for ΔE_α . In the limit $T \rightarrow 0$ we have to distinguish between the 3 regions

(1) $\varepsilon_d < 0$ $2\varepsilon_d + U < 0$

(2) $\varepsilon_d > 0$ $2\varepsilon_d + U > 0$

(3) $\varepsilon_d < 0$ $2\varepsilon_d + U > 0$

The limit $T \rightarrow 0$ of the β independent part of F generated by the c labelled single graphs tends to

$$\lim_{T \rightarrow 0} \sum_\alpha n_\alpha \Delta E_{\alpha(R.S)} = \Delta E^\alpha_{g(R.S)} \quad \text{in (1)}$$

$$= \Delta E^\alpha_{g(R.S)} \quad \text{in (2)}$$

$$= \frac{1}{2}\left[\Delta E^{\uparrow}_{g(R.S)} + \Delta E^{\downarrow}_{g(R.S)}\right] \quad \text{in (3)}$$

Clearly in the absence of an external magnetic field $\Delta E^{\uparrow}_{g(R.S)} = \Delta E^{\downarrow}_{g(R.S)}$

The dashed line connected graphs give contributions that go to zero in this limit. This is clear from the definition of the linking factors $M_n(\alpha_i, \alpha_j, \ldots \alpha_n)$. In the presence of a magnetic field h to lift the degeneracy in region (3), each factor of the type $\beta^n M_{n+1}$ must approach zero as $T \rightarrow 0$. However when $h = 0$,region (3) causes some difficulty, in this case all the contributions of this type must be grouped together before the limit $T \rightarrow 0$ is taken and then the above conclusion will follow. An example of this situation is provided by (4.23).

Thus the limit $T \rightarrow 0$ of $F^{(p)}$ can be written

$$\lim_{T \rightarrow 0} F^{(p)} = \Delta E^{(\alpha)}_{g(R.S)} + \varepsilon_\alpha + E^o_B \qquad (4.28)$$

where $\varepsilon_\alpha = 2\varepsilon_d + U - 2\mu$ in (1)

$= 0$ in (2)

$= \varepsilon_d - \mu$ in (3)

and $E_B^o = E_{g,B}^o - \mu\bar{N}$ where $E_{g,B}^o$ is the ground state energy for the non interacting band electrons. The label (p) in $F^{(p)}$ means 'perturbationally'.

We know on the other hand that if $F^{(e)}$ is the exact Free energy of the interacting system

$$\lim_{T\to 0} F^{(e)} = E_g - \mu\bar{N} \qquad (4.29)$$

where E_g is the exact ground state energy of the system. If the system is normal, or in other words if the adiabatic hypothesis is valid, then

$$E_g = \Delta E_{g(R.S)}^{(\alpha)} + \varepsilon_\alpha + E_{g,B}^o$$

where "α" is determined according to the 3 regions considered, and (4.29) is then identical to the ground state energy as determined from $F^{(p)}$ except for the replacement $\mu \to \varepsilon_F$ in $\Delta E_{g(R.S)}^{(\alpha)}$ where ε_F is the fermi level determined by the number of particles in the system. It turns out that in particular the effect of the neglected 'accidentally vanishing excitation energies' is to shift $\mu \to \varepsilon_F$ (section f). Thus if the system is normal then (4.28) and (4.29) are consistent when this allowance is made. On the other hand when adiabatic theory breaks down, $F^{(p)}$ no longer leads to the correct ground state energy.

Let us now consider the limit $T \to 0$ of F, where F is given by (4.21)

$$\lim_{T\to 0} F = E_{g,B}^o + \Delta E_g^{(\alpha)} + \varepsilon_\alpha - \mu\bar{N} \qquad (4.30)$$

where $\Delta E_g^{(\alpha)}$ is the $T \to 0$ limit of ΔE_α as given by (3.23). This

result is more general than (4.28) in two ways, firstly $\Delta E_g^{(\alpha)}$ is the ground state energy shift as given by the Brillouin-Wigner formula (3.23) and the correct solution of this equation, namely that which gives the least value for the ground state energy shift, is not necessarily the one obtained by the R.S expansion of (3.23), when the adiabatic hypothesis breaks down. Secondly, if we write

$$E_g^{(\alpha)} = \Delta E_g^{(\alpha)} + \varepsilon_\alpha + E^o_{g,B}$$

then if

$$E_g^{(\alpha_2)} < E_g^{(\alpha_3)} \qquad \text{in (3)}$$

the limit $T \to 0$ of (4.21) actually gives $E_g^{(\alpha_1)}$ and not $E_g^{(\alpha_2,\alpha_3)}$ as the true ground state energy in this region, whereas from (4.28) the factor n_α in the limit $T \to 0$ of $\sum_\alpha n_\alpha E_\alpha$ exponentially pushes the result to $E_g^{(\alpha_2,\alpha_3)}$ even if $E_g^{(\alpha_2,\alpha_3)} > E^{(\alpha_1)}$ in the region (3). Thus (4.21) indicates that the term by term analysis of the infinite series for F misses out the possibility of the sum giving rise to a qualitatively new result.

The greater generality afforded by (4.30) as opposed to (4.28) can have important consequences for this problem where it is known that as a result of the Kondo effect, anomalous behaviour occurs in the expansion of the physical parameters at low temperatures.

No anomaly is expected and none is found for the two functions $E^{(\alpha_1)}(T)$ and $E^{(\alpha_4)}(T)$, furthermore

$$\lim_{T \to 0} E^{(\alpha_1,\alpha_4)}(T) = E_g^{(\alpha_1,\alpha_4)} = E_{g(R.S)}^{(\alpha_1,\alpha_4)}$$

Adiabatic theory is valid in region (1) and (2) and the correct solution of (3.23) is the same as the perturbational or (R.S) solution corresponding to the unperturbed ground states $|\alpha_4\rangle\varphi_F$ and $|\alpha_1\rangle\varphi_F$ respectively which may also be written $|d_\uparrow d_\downarrow\rangle\varphi_F$ and $|00\rangle\varphi_F$.

The region of interest is (3) where one of the impurity states

lies below and the other above the 'Fermi level'. The unperturbed ground state $|d\sigma 0\rangle\varphi_F$ is doubly degenerate and in principle adiabatic theory is not valid. The temperature dependent function $\Delta E_\sigma(T)$ leads to the anomalies in the susceptibility at low T. The question of whether $\lim_{T\longrightarrow 0} \Delta E_\sigma(T) = \Delta E_{\sigma(S.C)} = \Delta\varepsilon^{\sigma}_{g(R.S)}$ must be looked at more carefully. (S.C) stands for 'self-consistent'.

The answer is provided by comparing the perturbation expansion of $\Delta E_\sigma(T)$ with the expansion of the Free energy in powers of J in the s-d model as given by Kondo[33]. Kondo explicitly calculated the fourth order dominant contribution to the Free energy by using the time integration method (3.5). He found a contribution behaving as Tlog(kT/W) and argued that there should be an infinite series which can eventually be written as

$$\delta F_{s-d} \propto \frac{T}{\left[1 - J\log(kT/W)\right]^3}$$

and diverges at $T = T_K$. Thus the expansion of F_{s-d} is not valid in $T \lesssim T_K$. Kondo's work suggests that when the lower order logarithmic terms are included in $F_{s-d}(T)$ such that the divergence at $T = T_K$ is removed, then the limit $T\longrightarrow 0$ of F_{s-d} can no longer be obtained from a T = 0 expansion of the ground state energy. More generally it can be said that

$$\lim_{T\longrightarrow 0} F_{s-d}(T) = E_g^{(s-d)} \neq E^{s-d}_{g(R.S)}$$

but in fact

$$E_g^{(s-d)} < E^{(s-d)}_{g(R.S)}$$

A direct comparison between $\Delta E_\sigma(T)$ in the limit $U\longrightarrow\infty$ and the Free energy in the s-d model shows that in the s-d region the two are essentially the same. Certainly we should expect a similar divergence

in $\Delta E_\sigma(T)$ perturbationally at $T = T_K$ and furthermore the exact $\Delta E_\sigma(T)$ in the limit $T \to 0$ will give the true ground state energy shift ΔE_g^σ which is less than $\Delta E_{g(R.S)}^\sigma$.

Thus the ground state energy shift in region (3) must be calculated self-consistently from the B.W formula

$$\Delta E_g^{\uparrow,\downarrow} = \sum_{p=1}^{\infty} \langle \downarrow,\uparrow \varphi | H_I \left(\frac{1}{\Delta E_g - \mathcal{E}} P H_I \right)^{p-1} | \varphi \uparrow,\downarrow \rangle \qquad (4.31)$$

where

$$|\varphi_\uparrow\rangle = |d_\uparrow 0\rangle \varphi_F$$
$$|\varphi_\downarrow\rangle = |d_\downarrow 0\rangle \varphi_F$$

and as a result of the Kondo effect, ΔE_g^σ can be thought of as having a 'non analytic part' which cannot be expanded by perturbation theory. Adiabatic theory is not valid in (3) and (4.31) has more than one solution the lowest one of which is not the perturbational or R.S solution.

The perturbation expansion for $\Delta E_\sigma(T)$ is strictly speaking not valid in $T \lesssim T_K$, however one can imagine to be in $T > T_K$ and obtain a result which can be continued to $T \lesssim T_K$. In principle $\Delta E_\sigma(T)$ can also be evaluated self-consistently from (3.23).

In $U \to \infty$, the limit $T \to 0$ of F can be summarized as follows:

$\varepsilon_d > 0$ i.e region (2)

$E_g = E_{g,\alpha_1}$. The ground state energy is obtained from $\Delta E_{\alpha_1}(T)$ in $T \to 0$, perturbationally (or non perturbationally). The exact many body ground state wave function has singlet symmetry, this follows from the adiabatic assumption.

$\varepsilon_d < 0$ i.e region (3)

In this case there are two possibilities

a) $E_g = E^{\sigma}_{g(S.C)} < E^{\sigma}_{g(R.S)}$

b) $E_{g(\alpha_1)} < E^{\sigma}_{g(S.C)}$ even in $\varepsilon_d < 0$

(b) would imply that even in $\varepsilon_d < 0$ the correct ground state energy is the one obtained by taking $|00\rangle \varphi_F$ as the zero order ground state. The evidence for this possibility is discussed in the next section, it must also be noted that this never arises in the s-d model because there are only two possible unperturbed ground states namely the pair of degenerate magnetic states $|\uparrow \varphi_F\rangle$ and $|\downarrow \varphi_F\rangle$. This could be an important difference between the s-d model and the Anderson model even in the U infinity limit.

In view of the significance of $E_{g(\alpha_1)}$ and $E^{\sigma}_{g(S.C)}$ we call

$$E_{g(\alpha_1)} = E^S_g$$
$$E^{\sigma}_{g(S.C)} = E^D_g$$

where S , D refer to 'Singlet' and 'Doublet' respectively.

d) <u>The limit $T \to 0$ of $\chi(T)$ in $U \to \infty$.</u>

It is now possible to investigate some of the consequences of the last section in relation to the $T \to 0$ limit for the susceptibility. From (4.1) the susceptibility can also be written

$$\chi(T) = \left[-kT \frac{\delta^2 Z}{\delta h^2} \frac{1}{Z} + \frac{kT \left(\delta Z/\delta h\right)^2}{Z^2} \right]\Bigg|_{h=0} \quad (4.32)$$

$$= \frac{\langle S^2_{z,tot} \rangle}{kT} - \frac{\langle S_{z,tot} \rangle^2}{kT} \quad (4.33)$$

Define $\Delta E_\alpha(T) + \varepsilon_\alpha + E^o_B = E_\alpha(T)$ (4.34)

$$E_{\alpha_1}(T) = E^S(T)$$
$$E_{\alpha_2,\alpha_3}(T) = E^D(T)$$

then

$$Z = Z_B^o \, e^{\beta(E_B^o)} \sum_\alpha e^{-\beta(E_\alpha(T))} \tag{4.35}$$

and

$$\chi(T) = \chi_A(T) + \chi_i(T) \tag{4.36}$$

where

$$\chi_A(T) = \chi_B(T) - \left.\frac{\delta^2 E_B^o}{\delta h^2}\right|_{h=o} \tag{4.37}$$
$$= \chi_B(T) - \chi_p$$

$$\lim_{T\to 0} \chi_A(T) = 0$$

$$\chi_i(T) = \left. \frac{\sum_\alpha \left[\left(\frac{\delta E_\alpha}{\delta h}\right)^2 \frac{1}{kT} - \left(\frac{\delta^2 E_\alpha}{\delta h}\right)\right] e^{-\beta(E_\alpha)}}{\sum_\alpha e^{-\beta(E_\alpha)}} \right|_{h=o}$$

$$- \left. \frac{\left[\sum_\alpha \left(\frac{\delta E_\alpha}{\delta h}\right) e^{-\beta(E_\alpha)}\right]^2 \frac{1}{kT}}{\left[\sum_\alpha e^{-\beta(E_\alpha)}\right]^2} \right|_{h=o} \tag{4.38}$$

Equations (4.36) and (4.38) give the susceptibility $\chi(T)$ calculated from the Free energy (4.21) which is exact except for the neglect of contributions of order 1/N and less. We are primarily interested in the low temperature limit for $\chi(T)$, in which case $\chi_A(T)$ can be neglected. In the absence of magnetic ordering and by rotational invariance of the Hamiltonian we put $\langle S_{z,tot} \rangle = 0$ at T = 0. Hence we can neglect the second term in $\chi_i(T)$ as given by (4.38) and it is clear that $\lim_{T\to 0} E_\alpha(T) = E_{g,\alpha}$ (=ground state energy)

Consider the situation $U = \infty$, $T \to 0$, $\varepsilon_d < 0$, and $E_\sigma^D < E_\sigma^S$ then in the low temperature limit $\chi(T)$ behaves as

$$\chi_i(T) = \frac{1}{2}\left[\frac{1}{kT}\left(\frac{\delta E_\sigma^D}{\delta h}\right)^2 - \left(\frac{\delta^2 E_\sigma^D}{\delta h}\right)\right]\Bigg|_{h=0} \qquad (4.39)$$

The divergence in $T \to 0$ is due to the first term which can be rewritten

$$\frac{1}{kT}\left[\mu_B \pm \frac{\delta \Delta E_\sigma}{\delta h}\right]^2\Bigg|_{h=0}$$

which is just the result obtained from the perturbation analysis and given by (4.25) , based on including the most important contributions in the limit $T \to 0$.

If $\left[\mu_B \pm \frac{\delta \Delta E_\sigma}{\delta h}\right]\Big|_{h=0}$ is interpreted as the effective moment' on the impurity , where μ_B is the magnetic moment of the localized spin and $\frac{\delta \Delta E_\sigma}{\delta h}$ corresponds to the antiparallel spin polarization around the impurity, it follows that for the effective moment to vanish in $T \to 0$

$$\left[\mu_B \pm \frac{\delta \Delta E_\sigma}{\delta h}\right]\Bigg|_{h=0} = \mu_{eff} \sim T^{\frac{1}{2}} \quad \text{as } T \to 0 \qquad (4.40)$$

$\frac{\delta \Delta E_\sigma}{\delta h}$ is determined from the equations (4.20) and (3.23), from which it is also possible to obtain approximate self-consistent results. However it is difficult to conceive how (4.40) could ever be satisfied unless one thinks of $\Delta E_\sigma(h,T)$ in terms of two separate parts (in $T \to 0$) e.g

$$E_\sigma(h,T) \sim \varepsilon_\sigma(h) + B(h,T) \qquad (4.41)$$

where $\varepsilon_\sigma(h)$ is a non analytic part describing the region close to the impurity and which is such that $\frac{\delta \varepsilon_\sigma(h)}{\delta h}\Big|_{h=0} = \mp \mu_B$ and $B(h,T)$ refers

to the rest of the system and is only weakly affected by the impurity such that $\left.\frac{\delta E(h,T)}{\delta h}\right|_{h=o} \longrightarrow 0$ as $T \longrightarrow 0$. The form given by (4.41) is suggested by the work of Kondo[54] on Suhl's theory [26] and Yosida[20], and essentially gives the picture of a "quasibound state" localized in the region of the impurity.

Now let us consider the situation

$$E_g^S < E_g^D \qquad \text{in} \qquad \varepsilon_d < 0$$

in this case the low temperature behaviour of $\chi(T)$ is determined by

$$\left[\frac{1}{kT} \left.\frac{\delta E^S(h,T)}{\delta h}\right|_{h=o} - \left.\frac{\delta^2 E^S(h,T)}{\delta h}\right|_{h=o} \right] \qquad (4.42)$$

$E^S(h,T)$ is well behaved and

$$\lim_{T \to 0} \left.\frac{\delta E^S}{\delta h}\right|_{h=o} = \left.\frac{\delta E_g^S(h,0)}{\delta h}\right|_{h=o}$$

remembering that E_g^S refers to the ground state energy of a many body singlet state (even in $\varepsilon_d < 0$), we have

$$\left.\frac{\delta E_g^S(h,0)}{\delta h}\right|_{h=o} = \mu_B \langle S_{z,tot} \rangle = 0$$

and the limit $T \longrightarrow 0$ of the susceptibility is given by

$$\chi(0) = \chi_p + (-1)\left.\frac{\delta^2}{\delta h^2}\left(\Delta E_{\alpha_1}(h,0)\right)\right|_{h=o} \qquad (4.43)$$

Naturally all this is saying is that if the exact ground state is a singlet, then the $T = 0$ susceptibility is finite.

The possibility that $E^S < E^D$ in $\varepsilon_d < 0$ has some relevance in view of the calculations made by Toulouse[55] for the ground state energy of the Anderson Hamiltonian in the limit $U \to \infty$. His approximate perturbational calculations for E_g^S and E_g^D in $\varepsilon_d > 0$ and $\varepsilon_d < 0$ led him to give an estimate of the behaviour of these quantities as a function of ε_d as shown schematically in Fig.62.

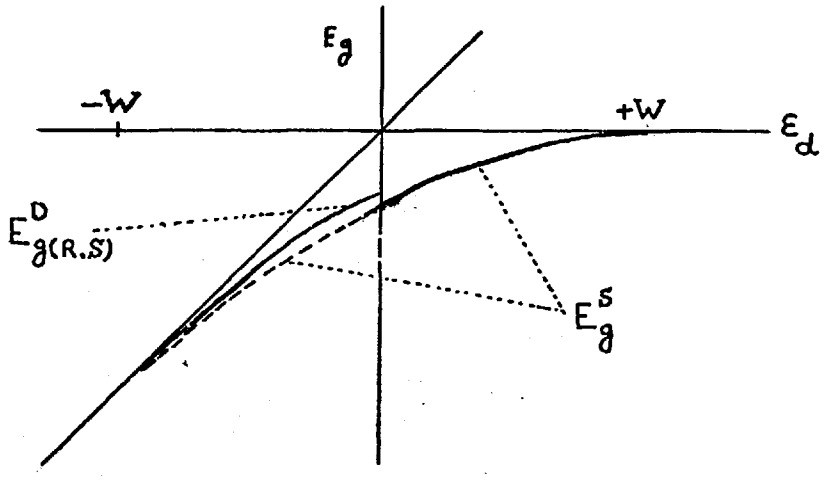


Fig.62
The behaviour of $E^D_{g(R.S)}$ and E^S_g as functions of ε_d according to Toulouse (reference 55). Dashed line is continuation of E^S_g into the region $\varepsilon_d < 0$.

From Fig.62 it can be seen that the analytic continuation of $E^S_g(\varepsilon_d)$ into the region $\varepsilon_d < 0$, denoted by the dashed line, is lower than the normal Doublet ground state energy $E^D_{g(R.S)}$. Toulouse concluded that the correct ground state energy in $\varepsilon_d < 0$ is given by E^S_g calculated in $\varepsilon_d < 0$, and that consequently the ground state many body wave function had singlet symmetry.

Toulouse's work raises the possibility that E^S_g is also less

than $E^{D}_{g(S.C)}$ in part of the region $\varepsilon_d < 0$, in which case it implies that the limit $T \to 0$ of $\chi(T)$ is given by (4.43) and is finite. If $\left[E^{D}_{g} - E^{S}_{g}\right] = kT_c$ where T_c is > 0, then in the limit of low temperature $\chi(T)$ can be written

$$\chi(T) = A + B\mu_B^2 \frac{e^{-(T_c/T)}}{T} \qquad (4.44)$$

where A, B are temperature independent , and the local moment is quenched exponentially as $T \to 0$. It must be remembered that the new structure predicted by the inequality

$$E^{S}_{g} < E^{D}_{g} \qquad \text{in} \qquad a < \varepsilon_d < 0$$

has been accounted for as a result of the exact inclusion of the dashed line connected graphs in the formula (4.21) for the Free energy.

e) Discussion

It appears that from the expression found for the Free energy (4.21), certain conclusions may be drawn as to the behaviour of $\chi(T)$ in the limit $T \to 0$ without having to evaluate the functions $\Delta E_\alpha(T)$ explicitly.

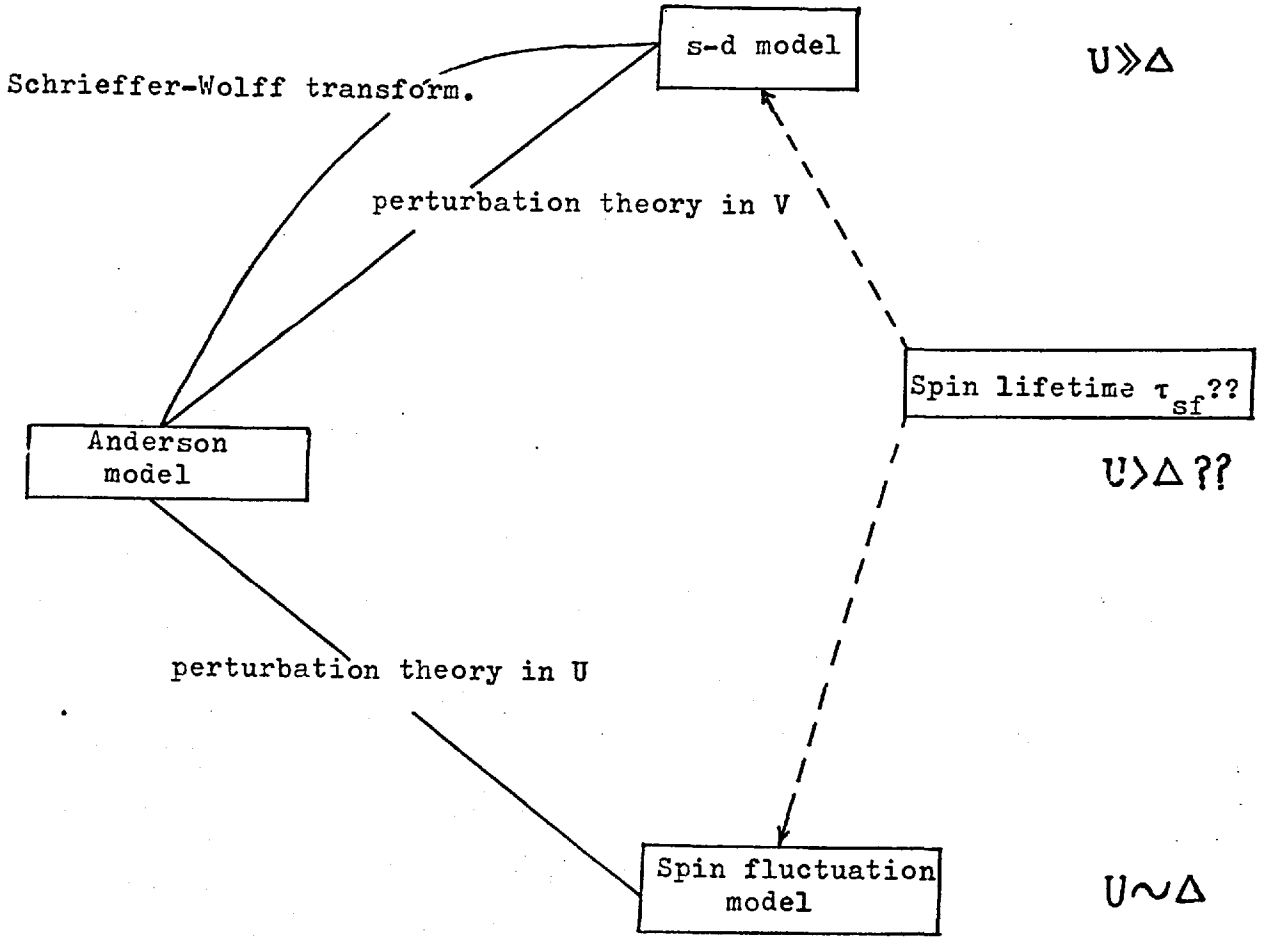
Toulouse [55], on the basis of his estimates for E^{D}_{g} and E^{S}_{g} (fig62) concluded that the ground state in the limit U infinity and for $\varepsilon_d < 0$ was of singlet symmetry. Such a conclusion however is not justified on the basis of a perturbation calculation of E^{D}_{g}. The close similarity between the temperature dependent functions $\Delta E_\sigma(T)$ and the Free energy in the s-d model indicates, in view of Kondo's calculations, that the limit $T \to 0$ of $\Delta E_\sigma(T)$ may not be calculated perturbationally, starting with the T=0 result. The true ground state for the pair of degenerate states $|d\sigma\rangle \varphi_F$ must be calculated self-consistently and will be lower than $E^{D}_{g(R.S)}$. Thus apparently the

question becomes focused on the relative magnitude of the self-consistent 'Doublet' solution and the Singlet solution in $\varepsilon_d < 0$. The latter possibilitiy is absent in the s-d model and is a feature of the Anderson model (in $U \longrightarrow \infty$).

It seems that one can deduce the following picture: in the region $\varepsilon_d \ll 0$ i.e in the s-d region, $E^D_{g(S.C)} < E^S_g$ and the limit $T \rightarrow 0$ of $\chi(T)$ is correctly given by (4.39) . It is difficult to see how $\chi(T)$ can be finite in $T \rightarrow 0$ unless one adopts the simple physical picture of a spin compensated singlet state formed by the localized spin and a conduction electron, localized near the impurity, the rest of the system being only 'weakly affected' by the presence of the impurity. This is a physical picture often adopted in s-d model calculations[45]. Better approximations involving more complicated many body proceeses tend to destroy the exact spin compensation near the impurity and and lead to a susceptibility which eventually diverges in $T \rightarrow 0$. A good starting point to obtain a self-consistent solution for $\Delta E_\sigma(T)$ may be to split it up into an analytic and non analytic part , the latter describing the region around the impurity.[33]

As ε_d moves closer to the Fermi level, at some stage E^S_g will be less than $E^D_{g(S.C)}$, the limit $T \rightarrow 0$ of $\chi(T)$ is then given by (4.42) or (4.43) and the local moment disappears exponentially as $T \rightarrow 0$. However at $T > T_c$ the temperature dependence of $\chi(T)$ is mostly determined by the magnetic component $\Delta E_\sigma(T)$, and at high temperatures this gives rise to a Curie law type behaviour. The possibility that $E^S_g < E^D_{g(S.C)}$ raises the question on the type of singlet structure $E^S_g(\varepsilon_d)$ describes in $\varepsilon_d < 0$. The spin flip effects are absent in $E^S(T)$ and it certainly does not seem to describe the kind of localized spin compensated state associated with the Kondo quasi-bound state. For E^S_g to be the ground state energy, ε_d would probably have to be in the band and quite close

to the Fermi level; even in this situation there will be spin flip effects (at finite temperatures) but the weak condensation energy and the importance of the lifetime effect could well mean that the 'Spin fluctuation model' is appropriate in this region even in U infinity.



This is in contrast to the $\varepsilon_d \ll 0$ situation where the localized spin is strongly correlated to 'a' conduction band electron and it is no longer possible to use the physical picture of a localized spin on which the effect of the many body interactions can be thought of as principally producing a finite lifetime.

Even in $U \longrightarrow \infty$ and $\varepsilon_d \ll 0$, there are however still difference between the Anderson model and the s-d model associated with the fact that in the former, the localized spin is not fixed and there will therefore always be a lifetime effect absent in the s-d model. In the perturbation theory presented here, this manifests itself in that there

are a considerably greater number of lower order logarithmic terms in the Anderson model calculations for the physical parameters. The technique developed in Chapter III is clearly equally suitable for the s-d model and future work on these lines should clarify further the question of the equivalence of the Anderson model and the s-d model.

f) The significance of contributions of O(1/N) and less to F

In Chapter III page 83, it was pointed out that the simple expression for Z and therefore F as given by (3.24) was only valid in the limit of a very large number of particles because effects of O(1/N) and less were neglected. In this section we briefly examine the significance of such contributions in the light of the work of R.Balian and C.de Dominicis[56] and R.Brout and F.Englert[57,58].

Consider for instance a contribution to Z in order V^4 as given by fig.37,

$$(-\beta/2\pi i)\int d\varepsilon.\frac{e}{\varepsilon}^{-\beta\varepsilon}\sum_{k_1,k_3}\frac{V^4 f_{k_1\sigma}(1-f_{k_3\sigma})\, n_{oo}}{4(\varepsilon+\varepsilon_{k_1\sigma}-\varepsilon_{d\sigma})^2(\varepsilon_{k_1\sigma}-\varepsilon_{k_3\sigma}+\varepsilon)} \qquad (4.45)$$

for $k_1 = k_3$ we obtain the contribution included in (3.24) and which is of O(1). When $k_1 = k_3$, (4.45) becomes

$$(-\beta/2\pi i)\int d\varepsilon.\frac{e}{\varepsilon}^{-\beta\varepsilon}\sum_{k_1}\frac{V^4 f_{k_1\sigma}(1-f_{k_1\sigma})\, n_{oo}}{(\varepsilon+\varepsilon_{k_1\sigma}-\varepsilon_{d\sigma})^2(4)} \qquad (4.46)$$

this is of order 1/N and is not included in (3.24). Obviously such contributions are not negligeable when the number of available states is small e.g as for the two atom problem where H_I is given by

$$H_I = V\sum_{\sigma}(c^+_{d\sigma}c_{o\sigma} + c^+_{o\sigma}c_{d\sigma})$$

When the ε integration is carried out in (4.46), we obtain as a contribution to F:

$$\sum_{k_1} \left\{ \frac{(-\beta) f_{k_1\sigma}(1 - f_{k_1\sigma})\, n_{oo}\, V^4}{(\varepsilon_{k_1\sigma} - \varepsilon_{d\sigma})^2 (2)} - \frac{f_{k_1\sigma}(1 - f_{k_1\sigma})\, n_{oo} V^4}{(\varepsilon_{k_1\sigma} - \varepsilon_{d\sigma})^3} \right\}$$

The first term gives a nonvanishing contribution in the limit $T \longrightarrow 0$ for $\varepsilon_d > 0$. Clearly this contribution has no equivalent in the ground state energy formula for $\varepsilon_d > 0$, (3.23) $\alpha = \alpha_1$, which differs from the true ground state energy formula i.e the Brillouin-Wigner expansion, by the replacement of μ by ε_F, where ε_F is the Fermi level and is determined by the number of particles in the system (fixed). In fact it can be shown that a large class of these terms must go to renormalize the Fermi functions f_k in such a way that in $T \longrightarrow 0$ μ is shifted to ε_F. The discussion of this point together with the proof is given in full by Balian and de Dominicis[56] when the zero order Hamiltonian is non interacting. A similar result would be obtained in this case as well. This may be seen quite easily by looking at the problem from another direction.

We recall that the partition function Z was calculated for a Grand canonical ensemble. In principle Z could also have been evaluated in a canonical ensemble, the former is very convenient because the thermodynamic Wick's theorem may be applied to the band states and the chemical potential is the exact one given by (3.3). The summation over the band states is unrestricted and this gives rise to the possibilities that e.g $k_1 = k_3$ as in (4.46) . On the other hand, had we worked in the canonical ensemble, i.e with a fixed number of particles N, then the thermodynamic Wick's theorem would no longer have applied and the temperature averages would have had to be evaluated under the restriction :

$$\sum_{k,\sigma}\left[n_{k\sigma} + n_{d\sigma}\right] = N$$

It is easy to see however that when these averages are evaluated, the contributions to order 1 would correspond precisely to the terms summed in (3.23), with the restrictions on the summations which exclude the vanishing of the denominators. The fermi functions would be

$$f_k = \frac{1}{e^{\beta(\varepsilon_k-\mu_o)}+1}$$

where μ_o is the unperturbed chemical potential which simply reduces to the Fermi energy ε_F, determined by the number of band electrons. Naturally there will also be contributions of O(1/N) and less which will go to renormalize the chemical potential to its correct value[53]. Coming back to the formulation involving the Grand canonical ensemble, we can state that in particular, inclusion of a class of contributions which are of O(1/N) and less will shift μ to μ-W($\underline{k}$) in f_k which is now written

$$F_k = \frac{1}{e^{\beta(\varepsilon_k+W_{\underline{k}}-\mu)}+1}$$

The new Fermi surface is defined by $\varepsilon_{k_F} + W_{k_F} = \mu$ and $W(\underline{k})$ is given by some self-consistency relation, any deformation of the Fermi surface arising out of the Kondo effect should be of negligeable importance in this particular problem. In fact to a good approximation we can replace μ by ε_F in all the results obtained in Chapters III and IV .

We can conclude that the O(1/N) and smaller contributions go to renormalize the Fermi functions for single particle excitations, they are not likely to be of great importance and the formula derived for F is a good description of the system. However this does not exhaust all the possible vanishing denominators (accidental), consider for

instance the $O(V^4)$ contribution to F which leads to the logarithmic term in the susceptibility

$$(V^4/4\pi i)\sum_{k_1,k_2,\sigma}\int_{\varepsilon}\frac{e}{\varepsilon}^{-\beta\varepsilon}\;\frac{n_{d\sigma}\,(1-f_{k_1\sigma})f_{k_2-\sigma}\;.\;d\varepsilon}{(\varepsilon+\varepsilon_{k_2-\sigma}-\varepsilon_{k_1\sigma}+\varepsilon_{d\sigma}-\varepsilon_{d-\sigma})(\varepsilon+\varepsilon_{d\sigma}-\varepsilon_{k_1\sigma})^2}$$

the possibility $k_1 = k_2$ leads to a $O(1/N)$ contribution proportional to

$$\sum_{k,\sigma}\int d\varepsilon.\frac{e}{\varepsilon^2}^{-\beta\varepsilon}\;\frac{n_{d\sigma}\,(1-f_{k_1\sigma})f_{k_1-\sigma}}{(\varepsilon+\varepsilon_{d\sigma}-\varepsilon_{k\sigma})^2}$$

and can be represented by the graph

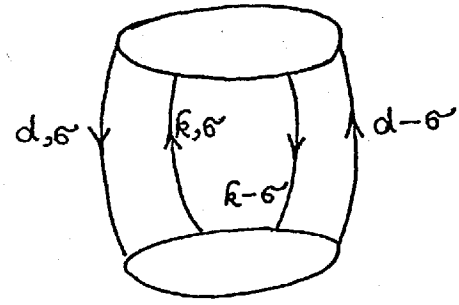


Fig.63

Unlike (4.46) which can be drawn

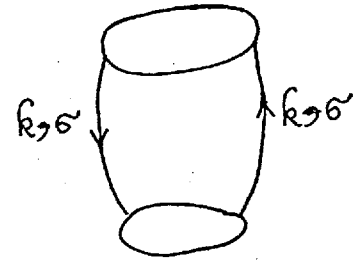


Fig.64

The graph corresponding to fig. 63 cannot be interpreted as a renormalization of the single particle distribution functions, although it is of

the same order as (4.46). A careful consideration of this point suggests that it actually renormalizes the two particle average

$$\langle c^{+}_{d\sigma} c_{k\sigma} c^{+}_{k-\sigma} c_{d-\sigma} \rangle \quad \text{to order } V^2 \quad \text{in e.g}$$

$$(-\beta/2\pi i) \int \sum_{k,\sigma} V^2 \frac{\langle c^{+}_{d\sigma} c_{k\sigma} c^{+}_{k-\sigma} c_{d-\sigma} \rangle}{\varepsilon(\varepsilon - \varepsilon_k + \varepsilon_d)} e^{-\beta\varepsilon} d\varepsilon \qquad (4.47)$$

and where the two particle average vanishes in zero order.

It appears therefore that a complete sum of the order 1/N and smaller contributions cannot be performed by introducing a self-consistent field $W(\underline{k})$ which acts on each particle individually[56], rather this would have to be a 'spin dependent field' in which case the temperature averages in (3.10) could no longer be decoupled in a simple way. Naturally this would then completely modify the form obtained for the partition function and the Free energy. An attempt to make the theory self-consistent along these lines, does not appear to be necessary in the limit $N \to \infty$ which is the situation one is interested in,, even though this question cannot be dismissed entirely in view of the argument due to Brout et al.[58] who pointed out that under certain conditions, namely when the system undergoes a transition to an ordered phase, contributions of O(1) may in fact become of O(N) (in this case it would be $O(1/N) \to O(1)$. In the impurity problem the question of an ordered phase in the usual sense does not arise, but clearly at low temperatures a kind of ordering does take place in the vicinity of the impurity for $\varepsilon_d \ll 0$ and a consistent description of this may require in the $T \to 0$ limit the consideration of the O(1/N) and smaller contributions to F, in particular those of the type (4.47).

CHAPTER V

SUMMARY AND CONCLUSIONS

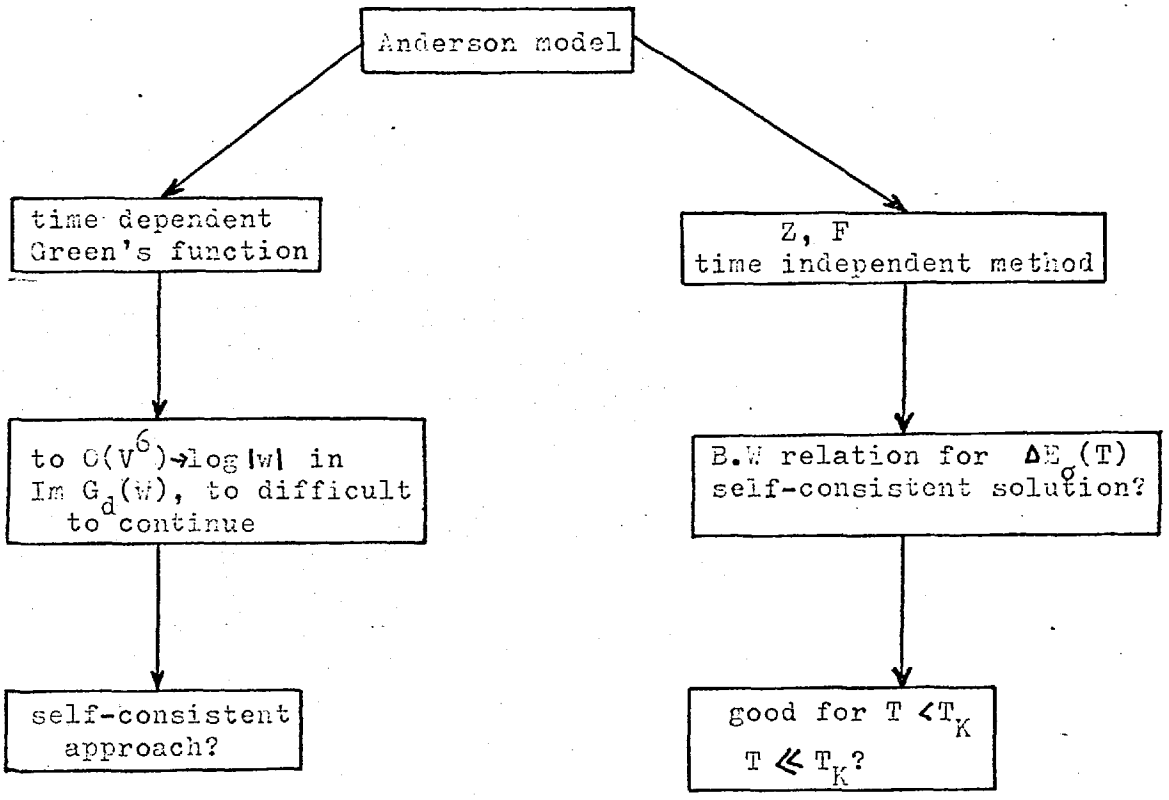
The theoretical treatments of the magnetic impurity problem were reviewed in Chapter I and particular attention was devoted to the two basic models that have been used to describe magnetic impurities in simple metals, namely the s-d model and the Anderson model. The s-d model in many ways gives results which are in good agreement with experiment, however the Anderson model commends itself by its greater generality and turns out to be 'equivalent' to the former in the region

$$\varepsilon_d - \varepsilon_F \ll \Delta$$
$$U + \varepsilon_d - \varepsilon_F \gg \Delta$$

but it is this particular region that the theoretical treatments used so far have been unable to descrbe beyond the first few orders of perturbation theory. Most of these were based on the well known connected graphical expansion of Field theory for the Green's function and dynamic susceptibility and despite their successes have failed to account for the s-d region. The most important recent development, the Spin fluctuation model, was outlined and critisized in Chapter II where it was also pointed out that the limitations of approximate theories for the magnetic impurity problem were closely connected to the use of the thermodynamic Wick's theorem. This indicated the necessity of developing an alternative approach in which the perturbation expansion would be carried out in powers of the mixing interaction while the correlations on the impurity were treated exactly.

The problem was approached in two ways, in Chapter II by means of a Green's function method and later using a time independent technique for the calculation of the Free energy. With the aid of the

Green's function it was possible to show how Abrikosov-Nagoaka type self energies would appear in the Anderson model, but the computational problems involved are so enormous that it is difficult to go beyond perturbation theory in particular for finite temperatures, although the method does indicate how a self consistent theory could be arrived at. Nevertheless it was possible to get an insight into the question of the validity of partial summations in linked graphical expansions in relation to the impurity problem.



The technique developed in Chapter III overcomes the computational problems normally encountered in perturbation theory when the thermodynamic Wick's theorem is not applicable. The expansion

obtained for Z (3.16) is a simple application of the method devised by C.Bloch and C. de Dominicis[51] but it has important consequences. It is particularly suited to the present problem where the restriction imposed by the exclusion principle is of fundamental importance and moreover reduces considerably the number of contributions that have to be evaluated. The representation in terms of the 'time ordered bubble graphs' was chosen to exploit this simplification in a direct manner, even though more familiar representations can also be used (section (a), Chapter III). The next step was to observe that the non overlapping graphs could be summed exactly and to reduce the calculation of Z, with the sole neglect of contributions of O(1/N) and less, to the self consistency relation

$$\Delta E_\alpha = g(\Delta E_\alpha)$$

and

$$\frac{Z}{Z_o} = \sum_\alpha n_\alpha e^{-\beta \Delta E_\alpha}$$

When Z is written in this form, it is a simple matter to obtain the perturbation expansion and the graphical representation for the Free energy, by writing F in the form (3.34) and calculating the linking factors using the cumulant expansion (2.32) in the limit when all the 'times' go to zero. The resulting expansion for F is given by (3.33) . The self-consistency relation (3.23) is particularly appealing for not only does it correspond to the Brillouin-Wigner formula giving the ground state energy shift in the limit $T \longrightarrow 0$, but it also gives the possibility of obtaining self-consistent results at finite temperatures In general it was shown that from an essentially perturbational result we were able to extend the theory into a form capable of going beyond perturbation theory.

With this technique it was possible to confirm the results

obtained by Scalapino for the static susceptibility and with the help of a connected graphical representation in the limit $U \to \infty$ generate the dominant logarithmic series for $\chi(T)$. Some general features of the perturbation expansion were analyzed and it was found that for $\chi(T)$, a perturbation theory based on including the most divergent terms as $T \to 0$ could at best lead to

$$\chi(T) = \chi_p + \frac{1}{kT}\left[\mu_B \pm \frac{\delta \Delta E_\sigma}{\delta h}\right]^2\Bigg|_{h=0}$$

in the 'magnetic region' $\varepsilon_d < 0 \quad 2\varepsilon_d + U \gg 0$. Using this it was shown that the lower order logarithmic terms could in fact be more divergent in $T \to T_K$ than the dominant series (4.12) .

The limitations of the perturbation formula for F were investigated in Chapter IV section (c) and it was found that (4.21) could lead to a ground state energy given by E_g^S for ε_d close to the Fermi level which would have drastic consequences on the behaviour of $\chi(T)$ in the limit $T \to 0$. It must also be noted that although the perturbation theory breaks down as $\varepsilon_d \to \mu$ (or $\varepsilon_d \to 0$), no difficulty is expected when the theory is viewed self-consistently via (3.23).

The time independent technique makes it easy to establish that the Free energy in the s-d model has the same qualitative behaviour as the function $\sum_\sigma n_{d\sigma}\, \Delta E_\sigma(T)$ in the limit $U \to \infty$, when J is identified via the Schrieffer-Wolff canonical transformation. In view of Kondo's calculation it follows easily that

$$\lim_{T \to 0} \Delta E_\sigma(T) \neq \Delta E^\sigma_{g(R.S)}$$

$$= \Delta E^\sigma_{g(S.C)} \quad \text{which is} < \Delta E^\sigma_{g(R.S)}$$

one should expect that $\left[E^\sigma_{g(R.S)} - E^\sigma_{g(S.C)}\right] \cong \varepsilon_L$

where ε_L is a non analytic part which cannot be expanded by perturbation theory and must be related to the condensation energy of the conduction electron(s). In particular a simple approximation for ε_L would give

$$\varepsilon_L = W\exp(-1/N(0)|J|) = kT_K$$

This argument is in contrast to Toulouse's suggestion[55] that

$$\left[E^{\sigma}_{g(R.S)} - E^{S}_{g}\right] \sim kT_K$$

and we conclude that the true ground state energy in the s-d region will be given by $\lim_{T\to 0} \Delta E_\sigma(T)$, despite the fact that in principle ΔE^{σ}_{g} refers to the ground state energy of a wave function with doublet symmetry. It seems that to obtain the correct singlet symmetry predicted by Mattis[36] would necessitate the inclusion of contributions of O(1/N) and less into F. Such contributions were neglected in the calculation of F and hence there would seem to be a contradiction, for on the one hand the fact that the exact ground state has singlet symmetry appears to be of great importance since it guarantees that the limit $T\to 0$ of $\chi(T)$ is finite, and on the other hand it was argued that such terms can be neglected in the limit of a large volume (or number of particles). This point can actually be explained as follows: in this problem where there is a single impurity in an 'infinite sea' of conduction electrons, the knowledge that the exact ground state wave function has singlet symmetry has little importance unless one also knows the type of singlet structure and the low energy excitations, for it turns out that the triplet states are only infinitesimally separated in energy from the singlet ground state[36]. The important aspect of $\Delta E_\sigma(T)$ is that it gives rise to the Kondo 'quasi-bound state' picture (at least in an approximate treatment of $\Delta E_\sigma(T)$), and one should expect exact compensation in this case to mean the cancellation of the moment in a finite (and small)

region around the impurity. Effects of O(1/N) and less on the other hand are associated with the redistribution of all the particles in the system with respect to the 'new Fermi surface' and should, in this problem, be negligeable in the limit as the volume goes to infinity (except for processes which as a result of ordering go from O(1/N) to O(1), if they exist at all).

The method presented in Chapter III and IV will be capable of dealing with the divergence at $T = T_K$ in the physical parameters, and in particular of generating results for $\Delta E_\sigma(T)$ and $\frac{\delta \Delta E_\sigma(T)}{\delta h}$ valid in $T \lesssim T_K$, but the question of the exact cancellation of the local moment in the s-d region is more difficult to decide on the basis of (4.39) . The possibility that $\chi(T)$ will diverge as $T \to 0$ in any approximate calculation because the inclusion of the more complex many body processes giving rise to the 'lower order divergences' destroys the approximate singlet bound state picture, cannot be dismissed. Nevertheless this is an important question which can be investigated further by using (4.20) and (4.39) .

The results and predictions given in Chapter IV are as far as one can go without evaluating the temperature dependent functions $\Delta E_\alpha(T)$ explicitly. They were mainly designed to provide an insight into the possibilities and shortcomings associated with the time independent technique in relation to the general theoretical problems encountered in the magnetic impurity problem. It can be seen that the most important difficulty that still remains is the question of the exact cancellation of the local moment in the s-d region. The answer to this question is by no means obvious from (4.39), and it is not surprising that the approximate non perturbational theories of Suhl and Nagaoka-Hamann-Bloomfield still predict a divergent $\chi(T)$ as $T \to 0$. One tends to suspect, on the basis of (4.39), that this is not simply a matter of

the breakdown of the approximations in $T \ll T_K$ but that it could well be associated with the inadequacy of the model itself in the very low temperature region. This is to be understood in the sense that to obtain a $\chi(T)$ even in qualitative agreement with experiment may require the consideration of very complex many body processes of much less importance than the interactions neglected in the host metal itself, in which case the resulting 'cancellation' may in fact have very little to do with the actual experimental reality. The point that should be stressed is that just because a particular model in some approximate calculations gives rise to results and concepts in agreement with experiment, need not necessarily mean that better and better approximations and in the final analysis the exact solution, will lead closer to the truth.

It appears that the time independent method presented in the last two Chapters is a powerful tool for the investigation of the Anderson model. The method essentially reduces to the calculation of $\Delta E_\alpha(T)$ for which a variety of techniques have been, and can be, devised, perturbationally and non perturbationally. It is clear that the applicability of the method is not restricted to the present problem but that it can be applied with advantage to the s-d Hamiltonian and should prove very effective for the two impurity problem as well. It has the disadvantage that it describes the physical parameters in the static limit, and gives no direct information on the dynamical aspects of the system. This restriction is particularly serious in view of the fact that recent experimental techniques have made it possible to observe 'directly' the dynamical characteristics of localized moments[45], and one should expect that a considerable part of future developments in the theory will be arrived at, both qualitatively and quantitatively, through the consideration of the time dependence of the physical observables.

APPENDIX (1)

Time Temperature Green's functions

The time Temperature Green's functions may be calculated as follows: consider for example the two particle Green's function $(-i)^2 \langle \{ c_{d\sigma_1}(t_1) c^+_{d\sigma_2}(t_2) c_{d\sigma_3}(t_3) c^+_{d\sigma_4}(t_4) \} \rangle$ which by definition may be expanded

$$G_2^{t,T}(t_1\sigma_1, t_2\sigma_2, t_3\sigma_3, t_4\sigma_4) = (-i)^2 \theta(t_1-t_2)\theta(t_2-t_3)\theta(t_3-t_4)$$

$$\langle c_{d\sigma_1}(t_1) c^+_{d\sigma_2}(t_2) c_{d\sigma_3}(t_3) c^+_{d\sigma_4}(t_4) \rangle + \ldots \text{etc}$$

where

$$\langle c_{d\sigma_1}(t_1) c^+_{d\sigma_2}(t_2) c_{d\sigma_3}(t_3) c^+_{d\sigma_4}(t_4) \rangle =$$

$$\frac{1}{\mathrm{Tr}\{e^{-\beta H_d}\}} \sum_{\alpha} e^{-\beta\varepsilon_\alpha} \langle \alpha | c_{d\sigma_1}(t_1) c^+_{d\sigma_2}(t_2) c_{d\sigma_3}(t_3) c^+_{d\sigma_4}(t_4) | \alpha \rangle$$

consider now the Fourier transform of $\theta(t_1-t_2)\theta(t_2-t_3)\theta(t_3-t_4) \times \cdots\cdots \rightarrow \langle \alpha | c_{d\sigma_1}(t_1) c^+_{d\sigma_2}(t_2) c_{d\sigma_3}(t_3) c^+_{d\sigma_4}(t_4) | \alpha \rangle$ with respect to the four time variables. This can be written

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \theta(t_1-t_2)\theta(t_3-t_4)\theta(t_2-t_3)\, e^{it_1(w_1+\varepsilon_\alpha-\varepsilon_n)}\, e^{it_2(-w_2+\varepsilon_n-\varepsilon_n)}$$

$$e^{it_3(w_3+\varepsilon_n-\varepsilon_n)}\, e^{it_4(-w_4+\varepsilon_n-\varepsilon_\alpha)} \langle \alpha | c_{d\sigma_1} | n_1 \rangle \langle n_1 | c^+_{d\sigma_2} | n_2 \rangle \langle n_2 | c_{d\sigma_3} | n_3 \rangle$$

$$\langle n_3 | c^+_{d\sigma_4} | \alpha \rangle \quad dt_1\, dt_2\, dt_3\, dt_4$$

Note: there is no summation over the intermediate states because

in this case there is only one possible intermediate state after each $c^{+}_{d\sigma_i}$ operator.

The time integrations may be carried out by making the change of variables

$$t_1 - t_2 = \tau_1 \quad , \quad t_2 - t_3 = \tau_3 \quad , \quad t_3 - t_4 = \tau_4 \quad , \quad t_1 + t_2 = \tau_2$$

and the result can be written

$$2\pi\delta(w_1+w_3-w_2-w_4)(i)^3 \quad \frac{1}{(w_4 - w_3 + \varepsilon_\alpha - \varepsilon_n + i\delta)(w_4 + \varepsilon_\alpha - \varepsilon_n + i\delta)}$$

$$\frac{1}{(w_1 + \varepsilon_\alpha - \varepsilon_n + i\delta)} \langle\alpha|c_{d\sigma_1}|n_1\rangle\langle n_1|c^{+}_{d\sigma_2}|n_2\rangle\langle n_2|c_{d\sigma_3}|n_3\rangle\langle n_3|c^{+}_{d\sigma_4}|\alpha\rangle$$

and may be defined as

$$K_\alpha(w_1\sigma_1, w_2\sigma_2, w_3\sigma_3, w_4\sigma_4)$$

The contributions corresponding to the different time orderings may be obtained from $K_\alpha(w_1\sigma_1, w_2\sigma_2, w_3\sigma_3, w_4\sigma_4)$ by permuations of the w's and appropriate modifications of α , n_1, n_2, n_3, ...etc. The 2-particle time temperature Green's function is calculated by grouping together the various contributions as indicated by the definition. It can be seen that even in this case, the algebra required to obtain $G_2^{t,T}$ is considerable. The 3,4 ... particle Green's functions are evaluated in a similar manner.

APPENDIX (2)

By definition, we have

$$G_2^T(iw_{n_1\sigma_1}, iw_{n_2\sigma_2}, \ldots\ldots, iw_{n_{2s}\sigma_{2s}}) = \int_0^{1/T} \ldots\ldots \int_0^{1/T} d\tau_1\, d\tau_2 \ldots\ldots d\tau_{2s}\; e^{i(w_n\tau_1)}$$

$$e^{-i(w_n\tau_2)} \ldots\ldots e^{-i(w_n\tau_{2s})}\, (-1)^s \langle T\{c_d(\tau_1)c^+_{d\sigma_2}(\tau_2) \ldots\ldots c^+_{d\sigma_{2s}}(\tau_{2s})\}\rangle$$

The time integrals in this case are much more difficult to evaluate because of the finite limit of the integrations. The simplest way is to expand the integrals in terms of the various time ordered averages and carry out the integrals directly, e.g for 2 particles and for $\beta > \tau_1 > \tau_2 > \tau_3 > \tau_4 > 0$ we have

$$\int_0^{1/T} d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \int_0^{\tau_3} d\tau_4 \quad \langle c_{d\sigma_1}(\tau_1)c^+_{d\sigma_2}(\tau_2)c_{d\sigma_3}(\tau_3)c^+_{d\sigma_4}(\tau_4)\rangle\, (-1)^2$$

$$e^{i(w_n\tau_1)}\, e^{i(w_n\tau_2)}\, e^{i(w_n\tau_3)}\, e^{i(w_n\tau_4)}$$

where

$$c^{\pm}_d(\tau) = e^{H_d\tau}\, c^{\pm}_d\, e^{-H_d\tau}$$

Similarly for the other possible time orderings . The complete G_2^T is then obtained by grouping the contributions together in the manner indicated by the definition. The computation is impossibly tedious beyond the 2 particle case.

APPENDIX (3)

Contributions to $C(V^6)$ from the (c) graphs in which all the spins are parallel and which correspond to (α_2,α_3)

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_3\sigma})f_{k_2\sigma}\,(-1)}{(\varepsilon_d-\varepsilon_{k_1})(\varepsilon_d-\varepsilon_{k_3})(\varepsilon_d+\varepsilon_{k_2}-\varepsilon_{k_1}-\varepsilon_{k_3})(\varepsilon_{k_2}-\varepsilon_{k_1})(\varepsilon_{k_2}-\varepsilon_{k_3})}$$

$$V^6 \sum_{k_1,k_2,k_4,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(f_{k_2\sigma})(f_{k_4\sigma})}{(\varepsilon_d-\varepsilon_{k_1})^3(\varepsilon_{k_2}-\varepsilon_{k_1})(\varepsilon_{k_4}-\varepsilon_{k_1})}$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_3\sigma})f_{k_2\sigma}}{(\varepsilon_d-\varepsilon_{k_1})^2(\varepsilon_{k_2}-\varepsilon_{k_1})^2(\varepsilon_d-\varepsilon_{k_1}-\varepsilon_{k_3}+\varepsilon_{k_2})}$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_3\sigma})(1-f_{k_1\sigma})f_{k_2\sigma}\,(-1)}{(\varepsilon_d-\varepsilon_{k_1})^3(\varepsilon_d-\varepsilon_{k_3})(\varepsilon_{k_2}-\varepsilon_{k_1})}$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_3\sigma})f_{k_2\sigma}\,(-1/2)}{(\varepsilon_d-\varepsilon_{k_3})^3(\varepsilon_d-\varepsilon_{k_1})^2(\varepsilon_{k_2}-\varepsilon_{k_1})}$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_3\sigma})(1-f_{k_1\sigma})f_{k_2\sigma}}{(\varepsilon_d-\varepsilon_{k_1})^2(\varepsilon_d-\varepsilon_{k_3})(\varepsilon_{k_2}-\varepsilon_{k_1})^2}$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_3\sigma})f_{k_2\sigma}\,(-1/2)}{(\varepsilon_d-\varepsilon_{k_1})^2(\varepsilon_d-\varepsilon_{k_3})^2(\varepsilon_{k_2}-\varepsilon_{k_3})}$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_3\sigma})f_{k_2\sigma}(-1)}{(\varepsilon_d-\varepsilon_{k_1})(\varepsilon_d-\varepsilon_{k_3})^3(\varepsilon_{k_2}-\varepsilon_{k_3})}$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_3\sigma})f_{k_2\sigma}(-1/2)}{(\varepsilon_d-\varepsilon_{k_1})(\varepsilon_d-\varepsilon_{k_3})^2(\varepsilon_{k_2}-\varepsilon_{k_3})^2}$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_2\sigma})(1-f_{k_3\sigma})(1/3)}{(\varepsilon_d-\varepsilon_{k_1})^3(\varepsilon_d-\varepsilon_{k_3})(\varepsilon_d-\varepsilon_{k_2})}$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_2\sigma})(1-f_{k_3\sigma})(2/3)}{(\varepsilon_d-\varepsilon_{k_1})(\varepsilon_d-\varepsilon_{k_3})^3(\varepsilon_d-\varepsilon_{k_2})}$$

$$V^6 \sum_{k_1,k_2,k_3,\sigma} \frac{n_{d\sigma}\,(1-f_{k_1\sigma})(1-f_{k_2\sigma})(1-f_{k_3\sigma})(1/2)}{(\varepsilon_d-\varepsilon_{k_1})^2(\varepsilon_d-\varepsilon_{k_2})^2(\varepsilon_d-\varepsilon_{k_3})}$$

One could think that there should be contributions to $\chi(T)$ behaving as $\log(T)$, $\left[\log(T)\right]^2$ ...etc as a result of the above terms, this is however not so and the anomalous contributions cancel when they have been grouped together.

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