Impurity states in Mott insulators
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1. Introduction. — We have recently studied the density of states and the mobility of a hole in a disordered magnetic insulator, in order to investigate the joint effect of atomic disorder and spin disorder on the properties of electron states in magnetic insulators [1].

Electron states in magnetic insulators have been discussed actively in the past few years [2], [3], [4]. In most magnetic insulators, the band theory of the conduction electrons breaks down because of the very strong Coulomb repulsion between the electrons. The most commonly used model Hamiltonian incorporates both the Coulomb repulsion and the kinetic energy; it uses a Wannier representation for the electron states and retains only the Coulomb repulsion between electrons on the same lattice site. Nagaoka [3], and Brinkman and Rice [4] have studied this model, the Hubbard model, in the atomic limit in which the transfer energy $t$ is taken as much smaller than the Coulomb repulsion; they have discussed the ground state, the density of states and mobility of an extra carrier. They have formulated the Hubbard model in this limit in terms of the number of possible paths on a lattice.

On the other hand, the problem of the propagation of a single particle in a random lattice has recently received considerable attention [5], [6], [7], while very little work at all has been devoted to the problem of interacting electrons in a random or disordered medium [8] to [11]. Our study of hole propagation in a random binary alloy is an attempt to treat one aspect of this problem in the strong coupling limit.

In this paper, we study in detail the specific aspects of this problem when the impurities are so dilute that it is a good approximation to treat them as independent scattering centers.

Thus, this paper deals with the properties of a magnetic insulator doped with a few impurities which are either donors or acceptors of electrons. The main feature of this problem is that the self energy of the impurity depends on the magnetic configuration in the host, so that for certain values of impurity potentials, the extra particle may be in a bound state for a given spin configuration, and in an extended state for another spin configuration. This renders possible
large magnetic field effects, such as large negative magnetoresistance.

In section 2, we summarize some known results in the pure case, essentially the work of Nagaoka’s [3] and Brinkman and Rice’s [4]. In section 3, we describe briefly some results for the random binary alloy [1]. The model for the dilute case and the conditions to bind a state for various spin configurations are described in section 4.1 and 4.2. A rigorous theorem for the ground state is derived in section 4.3. We show that Nagoaka’s result for the pure case can be generalized for the single impurity problem, i.e., the ground state is ferromagnetic for certain lattices. The physical meaning of this result is discussed in section 4.4, where we show that the bound hole stabilizes a ferromagnetic arrangement of spins, with a coupling strength which decreases exponentially with distance. In section 4.5, 4.6, 4.7, 4.8, 4.9, we study the displacement of the bound state when the spin configuration changes, the effect of a magnetic field, the possibility of a metal insulator transition, the transport properties. The final section is devoted to the experimental discussion.

Given the length of the present paper, we have left out for future publication [10] the detailed calculations corresponding to section 4.5, 4.6, 4.7, 4.8, 4.9, as well as a number of discussions dealing with the nature of the bound state when it is not outside the limits of the ferromagnetic band.

2. Some known results in the pure case. —

2.1 Model. — The simplest model one can work with is that of a nearly half filled tightly bound s-band, with infinite intra-atomic Coulomb repulsion between electrons [3]. This model, which neglects important features of d and f bands such as orbital degeneracy, intra-atomic exchange has the advantage of retaining the essential features of a magnetic insulator, namely the existence of unfilled atomic shells and of an overlap between atomic wave functions centered on neighbouring sites.

When no impurity is present, and when there are \( N - 1 \) electrons and \( N \) atoms, the Hamiltonian reduces to

\[
H_0 = P \sum_{i,j} t C^+_{i \sigma} C_{j \sigma} P
\]

where \( P \) projects on the subspace of wave functions

\[
\psi_{i \sigma} = (-1)^i C^+_{1 \sigma} C^+_{2 \sigma} \ldots C^+_{i-1 \sigma} C^+_{i+1 \sigma} C^+_{i+2 \sigma} \ldots C^+_{N \sigma} |0 \rangle
\]

where \(|0\rangle\) is the vacuum and \( \sigma \) denotes the spin configuration \( \sigma_1, \sigma_2, \ldots, \sigma_N \). \( t \) is the transfer integral between neighbouring sites. \( C^+_{i \sigma}, C_{j \sigma} \) are the creation (annihilation) operators of an electron of spin \( \sigma \) on site \( i, (j) \). In expression (2), the convention of sign \((-1)^i\) for \( \psi_{i \sigma} \) allows to discuss in a parallel way the case when the number of electrons \( N_e < N \) and the case \( N_e < N \) by considering holes in the former case instead of electrons in the latter case, and by changing the sign of \( t \). For sc and bcc lattices, one can divide the lattice into two sublattices, such that all the nearest neighbours of a lattice point on one sublattice belong to the other sublattice [3]. Then \( t \) changes sign if we introduce the phase factor \((-1)^i\) to the atomic wave functions at the lattice points on one sublattice.

Thus with the convention of sign chosen in (2), it can be assumed without loss of generality that \( N_e < N \) and that

\[
a) \ t > 0 \text{ for sc and bcc}, \\
b) \ t < 0 \text{ for fcc and hcp}.
\]

2.2 The ground state. — In the case \( 2.1 \) with \( N_e = N - 1 \), Nagaoka [3] has shown that the ground state is the ferromagnetic state with the maximum total spin \( S = S_{\text{max}} = \frac{1}{2} N_e \) and with energy \( E = -zt \), \( z \) being the number of nearest neighbours.

Nagaoka proves his theorem by two steps. First he shows that there is no state with \( E = -zt \) and secondly that there is no state with

\[
E = -zt \quad \text{and} \quad S < S_{\text{max}}.
\]

Let us sketch briefly his derivation. We introduce first the notation of a superlattice which consists of the set \( \{(i \sigma)\} \). In this superlattice each \( (i \sigma) \) represents a lattice point and \( (i \sigma) \) and \( (j \beta) \) are called nearest neighbours if

\[
\langle i \sigma | H | j \beta \rangle \neq 0.
\]

That is

\[
\langle i \sigma | H | j \beta \rangle = -t \quad \text{for} \quad \langle j \beta \rangle = n((i \sigma))
\]

\[
= 0, \quad \text{otherwise}
\]

where \( n((i \sigma)) \) denotes nearest neighbours of \((i \sigma)\). Each lattice point in the superlattice has \( z \) nearest neighbours as in the real lattice. The superlattice is equivalent to the real lattice for \( N_t = N_e \) and \( N_t = 0 \).

Let

\[
G_n^{i \beta}(\omega) \equiv \langle j \beta | i \sigma \rangle_\omega = \frac{\langle \psi_{i \sigma}, \Gamma_{\omega} \psi_{j \beta} \rangle}{\langle \psi_{i \sigma} | \Gamma_{\omega} | \psi_{i \sigma} \rangle}
\]

where \( \omega \) is a complex number in general. The poles of \( G_n^{i \beta}(\omega) \equiv \langle i \sigma | j \beta \rangle_\omega \) lie on the real axis and give the energy eigenvalues of the states with

\[
S > \left| \frac{N_t - N_t}{2} \right|
\]

Using the identity

\[
\frac{1}{\omega - H} = \frac{1}{\omega} + \frac{1}{\omega} \frac{1}{H} \frac{1}{\omega - H}
\]
we can drive the equation for $G_{ii}^{00}(\omega)$:

$$\omega G_{ii}^{00}(\omega) = \delta_{ij} \delta_{\alpha\beta} + \langle \psi_{ij} | H(\omega - H)^{-1} | \psi_{ii} \rangle$$

whence

$$\omega G_{ii}^{00} = \delta_{ij} \delta_{\alpha\beta} - \sum_{k} G_{kk}^{\alpha\beta}(\omega)$$

(5)

$$G_{ii}^{00}(\omega) = n_{i}(\omega)$$

Eq. (5) can be solved by successive iteration and $G_{ii}^{00}(\omega)$ is found to be

$$G_{ii}^{00}(\omega)^{-1} = G_{ii}^{*}(\omega)^{-1} = \omega - \Sigma_{i}^{*}(\omega)$$

(6)

where $A_{p}$ is the number of paths in which a particle starts from $(i_{0})$ in the superlattice and comes back to the same site after $p$ nearest neighbours steps without passing $(i_{0})$ on the way. As $Z_{p}$ is just the number of paths in which a particle starts from $(i_{0})$ and takes $p$ nearest neighbour steps without any restrictions, it is clear that $A_{p} < Z_{p}$.

Therefore $\Sigma_{i}^{*}(\omega)$ is absolutely convergent for real

$$\omega < - zt$$

Nagaoka notices that when $N_{f} = N_{e}$ and $N_{i} = 0$, the density of states for the holes reduces at once to that of the simple tight binding band for the one electron problem. In that case :

$$(i | i)_{\alpha}^{-1} = G_{ii}^{00}(\omega)^{-1} = \omega - \Sigma_{i}(\omega)$$

with

$$\Sigma_{i}(\omega) = \omega \sum_{p=2}^{\infty} \frac{A_{p}^{0}}{Z_{p}} \left( \frac{- zt}{\omega} \right)^{p}$$

(7)

$A_{p}^{0}$ is the number of paths in the real lattice. Since the lowest energy for this case is given by $- zt$, $G_{ii}^{00}(\omega)$ has no pole for $\omega < - zt$. This means that

$$\frac{1}{\omega} \Sigma_{i}(\omega) \neq 1 \quad \text{for} \quad \omega < - zt$$

Then Nagaoka proceeds by examining the modification of $\Sigma(\omega)$ when the spin configuration is modified from the fully ferromagnetically aligned state to some other spin state. Aside from the spin configuration obtained by a rotation of all axis of quantization on all sites by the same angle, it is fairly easy to show that any spin disorder amounts to closing some paths which were allowed in the ferromagnetic configuration. See for example figure 1. Thus there can be no zero in $G_{ii}^{00}(\omega)^{-1}$ for $\omega < - zt$. On the contrary all zeros in $G_{ii}^{*}(\omega)^{-1}$ shift towards the origin of energies when deviations from the fully ferromagnetically aligned state are introduced. Thus Nagaoka proved that the ground state was the ferromagnetic state with $N_{e} = N_{f}$ and $N_{i} = 0$ in the 2.1 case.

### I Ferromagnetic Configuration

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### II Antiferromagnetic Configuration

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![Figure 1](image-url)
Therefore one can rewrite (10) as a contour integral around the cut

\[ M_1^i = \frac{1}{N} \sum_c \left( \frac{\omega}{z} \right)^i G_r^i(\omega) \frac{d\omega}{2\pi i} \]  

(11)

where \( C \) denotes the contour shown in figure 2. Substituting the series (8) for \( G \) and deforming the contour to a circle of radius \( zt \) we find the result

\[ M_1^i = \frac{B_1^i}{zt}. \]

It remains to calculate the coefficients \( B_1^i \). This can be done by examining all possible paths and assigning a weight factor to each path depending on the spin configuration and calculating the weighted sum of all paths. This is done in detail in [4]. Figure 3 shows the paths which have been taken into account.

![Diagram](image1)

Fig. 2. — Contour used in evaluating the moments of the density of states function.

![Diagram](image2)

Fig. 3. — Possible paths in (i) second order, (ii) fourth order, (iii) sixth order.

From a knowledge of the moments, an approximate value of the band edge can be obtained by extrapolation, and it is found that the band is narrowed by approximately 20\% (R) and 25\% (AF) from the full (F) value. Brinkman and Rice argued that a band tail reaches all the way to the full ferromagnetic band width.

Walks with no closed loops.

If one examines the contribution to the moments, one finds that the dominant contribution is from the class of walks in which the hole completely retraces all steps. These walks which involve no closed loops enter with weight 1. Domb [12] refers to this class as walks with no closed configurations or walks on a Bethe lattice. This class is clearly not exact for the R configuration. For the AF configuration, however, the first correction to the moment expansion does not occur until twelfth order when the walk three times round the square becomes allowed.

It is possible to sum all walks with no closed loops and calculate analytically the corresponding Green’s function by using a technique similar to that used by Anderson in his paper on diffusion in random lattices [4], [5]. The simplest approximation to the self energy \( \Sigma^{(1)} \) is a walk to the nearest neighbour and an immediate return shown in figure 3 (i). Clearly

\[ \Sigma^{(1)}(\omega) = \frac{zt^2}{\omega}. \]  

(12)

The modification if we include a walk from the nearest neighbour to one of its nearest neighbours is obtained by modifying the denominator in \( \Sigma^{(1)} \) with a higher-order self energy. The next approximation is therefore

\[ \Sigma^{(2)}(\omega) = \frac{zt^2}{\omega - (z - 1) t^2/\omega}. \]  

(13)

In this way all paths which completely retrace themselves, i.e. those with no closed loops, are summed. The solution of (13) is simply:

\[ \Sigma(\omega) = \frac{zt^2}{\omega - \left(\frac{z - 1}{z}\right) \Sigma(\omega)} \]

whence

\[ \Sigma(\omega) = \frac{z\omega}{2(z - 1)} \left( 1 - \left( 1 - \frac{4(z - 1) t^2}{\omega^2} \right)^{1/2} \right) \]  

(14)

whence

\[ G(\omega) = \frac{1}{\omega} \left( 1 - \frac{z}{(z - 1)} \left( 1 - \frac{4(z - 1) t^2}{\omega^2} \right)^{1/2} \right)^{-1}. \]  

(15)

Figure 4 shows the resulting curve for the density of states, along with the results of the moment calculation.
Density of states obtained by a) (AF case) Legendre polynomial expansion to 12th order; b) (AF case) Legendre polynomial expansion in restricted region and c) from the sum of all walks with no closed loops.

2.4 TRANSPORT PROPERTIES. — Ohata and Kubo [13] have calculated the high temperature mobility by calculating the moments of the frequency dependent conductivity. With the same technique they also calculated the magnetoresistance and found a large negative magnetoresistance. The reason for the latter is simply that as spin alignment increases the probability for a given closed loop to be available for hole propagation increases. The probability for a closed loop of \( n \) steps to be available for hole propagation is

\[
(P_+(H))^{n-1} + (P_-(H))^{n-1}
\]

where

\[
P_±(H) = \left\{ 1 + \exp \pm gμ_B H/k_B T \right\}^{-1}
\]

is the probability for a spin to be aligned along (or opposite) the field.

If complete alignment is obtained, the mobility of the hole becomes infinite. The same effect causes a large change in the density of states upon application of an external field, as discussed by us [14].

Brinkman and Rice also calculated the mobility of a hole in the AF configuration and showed that the hole undergoes Brownian motion through the lattice.

3. Disordered magnetic insulators. — We have studied the density of states and the mobility of a hole in a disordered magnetic insulator, in order to investigate the joint effect of atomic disorder and spin disorder on the properties of magnetic insulators [1], [2].

3.1 THE MODEL. — The Hamiltonian for this problem is

\[
H = P \left\{ \sum_{i,σ} t_{ii} n_{iσ} + \sum_{i,j,σ} t_{ij} C^+_i C_{jσ} \right\} P
\]

where \( t_{ij} \) can take two values \( E_A \) or \( E_B \) according to whether site \( i \) is occupied by an A atom or by B atom. \( t_{ij} \) is taken to be a constant if \( i \) and \( j \) are nearest neighbours, zero otherwise.

3.2 THE GROUND STATE. — We have proved that Nagaoka's theorem remained true in the presence of atomic disorder; the derivation of this theorem follows closely the proof given by Nagaoka in the pure case [2].

3.3 DENSITY OF STATES. — Using the retraceable Path Approximation, we have computed the density of states of the extra hole for the F, AF and R configurations in the presence of atomic disorder. Writing the Green’s function

\[
G^{±}_n(ω)^{-1} = ω + E_i - Σ^{±}_n(ω).
\]

The general expression for \( Σ_n^±(ω) \) is

\[
Σ_n^±(ω) = \sum_{i_1, i_2} \frac{(-t_{i_1})}{ω + ε_i} + \sum_{i_1} \frac{(-t_{i_1})}{(ω + ε_i) \left( ω + E_A \right)} + \cdots
\]

\[
+ \sum_{i_1, \ldots, i_q} \frac{(-t_{i_1})}{(ω + ε_i_1) \cdots (ω + ε_i_q)} + \cdots
\]

where the \( q \)th term corresponds to all paths in which a particle starts from \( (i_0) \) in the super lattice and comes back to the same site after \( q \) nearest neighbour steps, without passing \( (i_n) \) on the way.

In eq. (17) and (17') the origin of energies is determined by the condition

\[
N_A ε_A + N_B ε_B = 0
\]

where \( N_{A,B} \) is the number of atoms of species A, B.

We obtain the simplest approximation to the self energy \( Σ^{(1)}(ω) \)

\[
Σ^{(1)}(ω) = z\frac{1}{σ} \left( \frac{1}{ω + E_A} + \frac{1-σ}{ω + E_B} \right).
\]

From (18) one obtains by iteration a continuous fraction which we can solve easily, obtaining a 3rd degree equation for \( Σ(ω) \):

\[
Σ(ω) = z\frac{1}{σ} \left( \frac{1}{ω + E_A} + \frac{1-σ}{ω + E_B} \right)
\]

\[
Σ(ω) = z\frac{1}{σ} \left( \frac{1}{ω + E_A} + \frac{1-σ}{ω + E_B} \right)
\]

\[
= 0.
\]

The density of states is computed from

\[
G(ω) = \frac{1}{ω + E_A - Σ(ω)} + \frac{1-σ}{ω + E_B - Σ(ω)}.
\]

We have also computed the density of states using the Coherent Potential Approximation [6], and we have shown that the two approximations give very similar results when closed loops are neglected. We
show on figure 5 a typical result for the density of states in a concentrated alloy.

FIG. 5. — Density of states for F and AF configuration for a concentrated alloy with δ = (EA - Eb)/2t.

3.4 TRANSPORT PROPERTIES IN THE DISORDERED MAGNETIC INSULATOR. — Atomic disorder does not change significantly the picture of the Brownian motion through the lattice, at least for energies above the mobility edge. In the region of Anderson localization one has thermally activated hopping [2], [15]. The condition for localization in Anderson’s sense differs in the F configuration and in the AF one. In the latter configuration, one may look for the probability that the self energy Σ(ω) converges using the Retraceable Path Approximation. This is just what Thouless investigated, although his paper deals with the one electron problem [7]. The condition for Anderson’s localization in the F configuration compared to the AF one is still an open question in the concentrated alloy problem. Localization is certainly more difficult in the F configuration.

3.5 COMMENTS. — We have found it necessary to investigate the limiting case of very dilute impurities, so as to check the validity of the results obtained for the concentrated alloy. In the following sections we show that the theorem on the ground state holds even when the impurity is strongly attractive (or repulsive), and that this has interesting consequences on the magnetic environment of the impurity, as well as on the transport properties; we shall show that the change in the impurity self energy with the spin configuration in the host may even provide a new mechanism for a sort of metal-insulator transition, when, upon application of a magnetic field or upon ordering in the host, the impurity level collapses in the band.

4. Impurity states and strong correlations in narrow energy bands. — 4.1 MODEL. — We are now going to investigate the effect of a point scattering potential on the properties of the pure system discussed in part 2. This is a limiting case of the system discussed in part 3.

The perturbed Hamiltonian is

\[ H' = P \left\{ t_0(n_{0t} + n_{0i}) + t \sum_{i,j} C_{i\sigma}^{+} C_{j\sigma} \right\} P. \]  

For simplicity, we now redefine the origin of energies so that the kinetic energy of a state \( \psi_{i\alpha} \) where \( i \neq 0 \) is zero when \( t_{ij} = 0 \), while the kinetic energy of a state \( \psi_{0\alpha} \) is \( -t_0 \). This amounts to adding to the Hamiltonian a constant term \( -t_0 \) so that now

\[ H' = P \left\{ t_0(n_{0t} + n_{0i} - 1) + t \sum_{i,j} C_{i\sigma}^{+} C_{j\sigma} \right\} P. \]  

In a first stage, we neglect any change in the transfer integral between the impurity site and neighbouring sites. This would introduce a term

\[ \delta t \sum_{k} C_{0k}^{+} C_{kk} + \text{cc} \]

where \( k \) is nearest neighbour to the origin. We also neglect orbital degeneracy. Both terms will be discussed in the Appendix I.

4.2 DENSITY OF STATES. — (i) When all electron spins are aligned (F configuration) the problem reduces at once to the familiar Slater-Koster impurity problem [16] in the otherwise unperturbed tight binding band. The central site Green’s function is

\[ G_{OF}(\omega) = \left\langle \psi_{OF} \left| \frac{1}{\omega - H'} \right| \psi_{OF} \right\rangle \]  

where \( \psi_{OF} \) is the wave function describing the fully aligned spin state with the hole sitting at the origin. Calling \( F_{0}(\omega) \) the central site Green’s function in the absence of scattering center, we have the well known result:

\[ G_{OF}(\omega) = \frac{F_{0}(\omega)}{1 + t_0 F_{0}(\omega)} \]  

with

\[ F_{0}(\omega) = \frac{1}{N} \sum_{k} \frac{1}{\omega - \epsilon_{k}} \]

\( \epsilon_{k} \) is the dispersion relation corresponding to the transfer integral \( t \) in a given lattice. We can write (23) in a different manner, using eq. (17) and (17')

\[ G_{OF}^{-1}(\omega) = \omega + t_0 - \Sigma_{0}(\omega) \]

and

\[ \Sigma_{0}(\omega) = \omega \sum_{p} \left( \frac{\delta_{p}}{\omega + \epsilon_{p}} \right) \left( \frac{z(1)}{\omega} \right)^{p} \]  

with the same notations as in eq. (8).

From the knowledge of \( F_{0}(\omega) \), one can determine the minimum impurity potential strength \( \delta_{0} \) neces-
sary to split a bound state from the bottom of the band. The equation for $t'_0$ is

$$t'_0 F_0(-z t) + 1 = 0. \quad (24)$$

In the fcc case one finds

$$t'_0 = + 0.68 \ W \quad (24')$$

where $W$ is the half band width $z t$.

— When $t_0 > t'_0$ a bound state is extracted from the band. The energy $E^F_0$ is given by the equation

$$t_0 F_0(E^F_0) + 1 = 0$$

or by the equivalent equation obtained from (23) :

$$E^F_0 + t_0 - \Sigma^F_0(E^F_0) = 0 \quad (24'')$$

with

$$\Sigma^F_0(E^F_0) = E^F_0 \sum_{p=2}^{\infty} \left( \frac{A_0}{\xi^p} \right) \left( \frac{-z t}{E^F_0} \right)^p.$$

— When $t_0 < t'_0$, the impurity potential perturbs the density of states. The contribution of the impurity center to the density of states is given by $\text{Im} \ G^F_0(\omega + i \eta)$.

(ii) When the spin configuration is AF or R, or generally different from the completely ferromagnetic configuration, one can derive an equation for the scattered Green’s function $G^\delta_0(\omega)$ using the identity

$$\frac{1}{\omega - H_0 - V_0} = \frac{1}{\omega - H_0} \frac{1}{\omega - H_0 - V_0}.$$

This yields, with $V_0 = t_0(n_{0\uparrow} + n_{0\downarrow} - 1)$

$$\langle i \tau_1 | \frac{1}{\omega - H_0 - V_0} | j \beta_j \rangle = \langle i \tau_1 | \frac{1}{\omega - H_0} | j \beta_j \rangle + \langle i \tau_1 | \frac{1}{\omega - H_0} V_0 | \omega - H_0 - V_0 | j \beta_j \rangle$$

$$= \langle i \tau_1 | \frac{1}{\omega - H_0} | j \beta_j \rangle + \sum_{m \neq m} \langle i \tau_1 | \frac{1}{\omega - H_0} | l \beta_j \rangle \langle l \beta_j | V_0 | m \beta_m \rangle$$

using

$$\delta_{l \beta_j} \langle m \beta_m | \omega - H_0 - V_0 | j \beta_j \rangle = - \delta_{m \beta_m} \delta_{l \beta_j} t_0$$

we obtain

$$G^\delta_0(\omega) = G^{0\delta}_0(\omega) - t_0 \sum_{m} G^{0\delta}_0(\omega) G^{\delta\gamma}_0(\omega). \quad (25)$$

where $G^{0\delta}_0(\omega)$ is the Green's function for $t_0 = 0$. The sum $\sum_{m}$ extends over all spin configurations corresponding to the hole sitting at the impurity site. The equation for the impurity site Green's function shows that the scattering potential couples states corresponding to different spin configurations with the hole sitting at the impurity site:

$$G^{\gamma\delta}_0(\omega) = G^{0\delta}_0(\omega) - \sum_{m} G^{0\delta}_0(\omega) G^{\gamma\delta}_0(\omega). \quad (25)$$

For example, a walk around the square path shown in figure 1 connects configurations (a) and (b) in the AF case. States corresponding to different spin configurations can only be connected through closed loops. A Retraceable Path can only connect a given spin configuration with itself. In the vicinity of the R or AF configuration, we have seen that in the pure case, closed loops are strongly suppressed compared with the F case in the self energy, i.e. in $G^\gamma_0(\omega).$ Thus it is consistent with the Retraceable Path Approximation used by Brinkman and Rice in the pure case [4] to neglect non diagonal Green’s functions in (25), i.e., all processes which couple different spin configurations.

Then eq. (25) becomes

$$G^\delta_0(\omega) = G^{0\delta}_0(\omega) - t_0 G^{0\delta}_0(\omega) G^{0\delta}_0(\omega)$$

$$= \frac{G^{0\delta}_0(\omega)}{1 + t_0 G^{0\delta}_0(\omega)}. \quad (26)$$

Thus, within the approximation that all loops are neglected in the evaluation of $G^{\gamma\delta}_0(\omega)$, the problem reduces also to the Slater-Koster problem of a single impurity in an orbitally non degenerate band, the unperturbed Green’s function being given by eq. (15).

An equivalent expression for $G^\delta_0(\omega)$ can be obtained from eq. (17) and (17'), and eq. (14), namely

$$G^\delta_0(\omega) = - \frac{z \omega}{(z - 1) 2} \left( 1 - \frac{4(z - 1) + 2}{\omega^2} \right)^{1/2}.$$
In particular, the minimum impurity potential strength necessary to split a bound state from the bottom of the spin disordered band is given by

$$t_0^R G_0^{OR}(- \alpha z t) + 1 = 0$$ (27)

where $G_0^{OR}(\omega)$ is the unperturbed Green's function in the Retraceable Path Approximation and $\alpha z t$ is the band edge in this approximation (i.e., $\alpha \sim 0.75$).

Using eq. (15) for $G_0^{OR}(\omega)$, one finds

$$t_0^R = +0.3 W.$$

Thus a much weaker impurity potential is needed to localize a particle in a half filled band in the presence of spin disorder (or AF order) than in the case of a ferromagnetic configuration, i.e., in the single particle localization problem [5]. A more careful treatment of the AF spin configuration and of the R spin configuration shows that the band width, as obtained from

$$\quad \omega_0 \simeq \left( \lim_{s \to \infty} \frac{M_{s+1}}{M_s} \right)^{1/2}$$

differs for the two spin configurations. Taking into account the various spin factors which are attached to the closed loops, Rice and Brinkman [4] found

$$W_{\text{AF}} = 0.75 z t$$

while the R half band width is

$$W_R = 0.80 z t$$

about 5% larger than $W_{\text{AF}}$.

We can now approximately determine the impurity potential needed to localize a state in the AF configuration, by assuming the band shape to be correctly given by the Retraceable Path Approximation: we look for the value $t_{\text{AF}}^0$ of $t_0$ necessary to localize a state at $\omega = W_{\text{AF}}$. This is approximately given by

$$t_{\text{AF}}^0 G_0^{OR}(- W_{\text{AF}}) + 1 = 0$$

whence one finds

$$t_{\text{AF}}^0 \simeq 0.3 W.$$

Similarly, the value $t_{\text{R}}^0$ necessary to localize a state at $\omega = W_R$ is approximately given by

$$t_{\text{R}}^0 \simeq 0.37 W$$

since $W_R > W_{\text{AF}}$. It is not surprising that $t_{\text{R}}^0 > t_{\text{AF}}^0$ although the fact that a random spin configuration looks less disordered from the point of view of localization than an AF one is not evident at first sight. When $t_{\text{R}}^0 > t_0 > t_{\text{AF}}^0$ a bound state is extracted from the AF band, but no bound state is extracted from the spin disordered band.

When $t_0 < t_{\text{R}}^0$ a bound state is extracted from the spin disordered band. The energy $E_{\text{R}}^R$ of the bound state is given by

$$t_0 G_0^{OR}(E_{\text{R}}^R) + 1 = 0.$$ (28)

An equivalent expression is obtained from eq. (17) and (17) :

$$E_{\text{R}}^R + t_0 - \Sigma_{\text{R}}^0(E_{\text{R}}^R) = 0$$

with

$$\Sigma_{\text{R}}^0(E_{\text{R}}^R) = E_{\text{R}}^R \sum_{p=2}^{\infty} \left( \frac{A_{\text{R}}^p}{z^p} \right)^p.$$

where $A_{\text{R}}^p$ is the number of paths such that the particle leaves the origin and returns after $p$ steps along a Retraceable Path.

The exact expression for $\Sigma_{\text{R}}^0(\omega)$ in eq. (28) includes terms corresponding to closed loops such that the spin configuration is restored after the hole has completed the path. Thus, for example, in an antiferromagnetic configuration such as that represented on figure 1a $\Sigma_{\text{AF}}^0(\omega)$ contains, to eighth order in $t$, terms of the form

$$\frac{t_{12}^R}{o}\frac{1}{(o + t_0)^2}$$

such a term represents the effect, to eighth order in $t$ of the non diagonal Green's functions neglected in eq. (25), obtained by an anticalkwise return back to the origin, after a clockwise walk around the square, $\Sigma_{\text{AF}}^0(\omega)$ also contains, to twelfth order in $t$, terms of the form

$$\frac{t_{12}^R}{o^4}\frac{1}{(o + t_0)^2}.$$

Such a term represents the effect, to twelth order in $t$ of the non diagonal Green's functions obtained by restoring the original spin configuration after walking three times around the square in the same direction. In the case of a Random configuration, the exact expression for $\Sigma_{\text{R}}^0(\omega)$ also contains lower order terms which correspond to closed loops which are forbidden in an AF configuration, but which have a certain probability $p$ of being open for hole propagation. $p$ is just the probability that all spins are aligned along the loop.

4.3 Ground state. — We shall now prove that the general theorem derived in the case of a narrow almost half filled band with infinite intra-atomic interactions and random atomic disorder also holds for the case of a single impurity, including when the impurity potential subtracts a localized state from the band [17]. The general theorem states that the ferromagnetic state with the maximum total spin is the ground state for simple cubic and body centered cubic structures with $N_e = N - 1$ as well as for face centered cubic and hexagonal closed packed structures with $N_e = N + 1$.

4.3.1 Case of a localized state. — Let us first of all investigate the case of an impurity potential
repulsive enough to bind a hole in the ferromagnetic configuration, i.e. \( t_0 > t_0' \).

If the band was infinitely narrow, i.e. if \( t = 0 \) then the bound state has energy
\[
E_{B}^t = - t_0
\]
when the band width \( W = 2 \pi t \) is finite and in the ferromagnetic configuration, the localized state has a self energy
\[
\Sigma_0^t(E_{B}^t) = E_{B}^t \sum_{p=\pm} A_{p}^{0} \left( \frac{- z t}{E_{B}^t} \right)^{p}.
\]  
(29)

We have of course
\[
E_{B}^t < - t_0.
\]

Since \( A_{p}^{0} < z^p \), the series (29) converges absolutely whenever \( t_0 > t_0' \). First notice that one can obtain from the state of maximum total spin \( S = N_e / 2 \) and maximum component \( S_z = S = N_e / 2 \), i.e. the state :
\[
\left| S = \frac{N_e}{2}, \quad S_z = \frac{N_e}{2} \right> = C_1^+ \cdots C_{0}^{+1} \cdots C_{0}^{+1} \cdots C_{0}^{+1} \cdots 0 \right>
\]
all other states of maximum spin \( S = N_e / 2 \) by repeated application of the spin lowering operator
\[
S_- = (N - 1)^{-1/2} \sum_i C_i^- C_i^+
\]
on
\[
\left| S = \frac{N_e}{2}, \quad S_z = \frac{N_e}{2} \right>
\]
However the operation of \( S_- \) on
\[
\left| S = \frac{N_e}{2}, \quad S_z = \frac{N_e}{2} \right>
\]
does not alter \( \Sigma_0^t(\omega) \), as can be seen when performing a counter rotation of the same angle on the axis of spin quantization of each atomic site. Thus one knows all the states of energy \( E_{B}^t \), spin \( S = N_e / 2 \) and spin projection \( S_z = N_e / 2 \).

Let us now prove the theorem, following closely Nagaoka's derivation.

We consider the general case of arbitrary numbers of \( N_t \) and \( N_s \). Let us introduce
\[
v_{sp}(\omega) = \sum_{\beta} \left( \frac{C_{\beta}^{0}}{\omega} \right)^{p} \left( \frac{- z t}{\omega} \right)^{p}.
\]  
(30)

where \( C_{\beta}^{0} \) is the number of paths in which a particle starts from \((0, \alpha_0)\) and arrives at \((0, \beta_0)\) after \( p \) nearest neighbour steps, without passing \((0, \gamma_0)\) on the way. \( v_{sp}(\omega) \) is also absolutely convergent for \( \omega < - z t \).

It is clear that \( v_{sp}(\omega) > 0 \) for \( \omega > - z t \). Eq. (31) follows from \( \Sigma_{sp} \) \( C_{sp}^{0} = A_{sp}^{0} \), which is proved by watching the motion of the hole in each path contributing to \( C_{sp}^{0} \).

Using \( v_{sp}(\omega) \) we rewrite \( \Sigma_{0}(\omega) \) as
\[
\frac{1}{\omega} \Sigma_{0}(\omega) = v_{sp}(\omega) + \left( \frac{\omega}{\omega + t_0} \right) \sum_{\beta} v_{sp}(\omega) v_{\beta s}(\omega) +
\]
\[
\frac{\omega}{\omega + t_0} \sum_{\beta} v_{sp}(\omega) v_{\beta s}(\omega) v_{\gamma s}(\omega) + \cdots
\]
(32)

where the \( n \)th term is the contribution from the paths in which the particle passes the origin \( (n - 1) \) times on the way. Each time the particle passes the origin, it sees a potential \(- t_0 \) instead of the lattice potential.

Using eq. (31) repeatedly, we can rewrite eq. (32) as follows :
\[
\omega + t_0 - \Sigma_{0}(\omega) = \omega (1 + \frac{\omega}{\omega + t_0} \sum_{\beta} v_{sp}(\omega) + \left( \frac{\omega}{\omega + t_0} \right)^{2} \sum_{\beta} \sum_{\gamma} v_{sp}(\omega) v_{\beta s}(\omega) v_{\gamma s}(\omega) + \cdots.
\]  
(34)

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Because of eq. (24") and eq. (29), we know that 
\( \omega (\omega + t_0) > 0 \) for \( \omega = E_B^F - t_0 \). Furthermore we know, from (31), that,
- for \( \omega < E_B^F \), \( \frac{\omega + t_0}{\omega} > \sum_{\beta} v_{s \beta}(\omega) \) and that
- for \( \omega > E_B^F \), \( \frac{\omega + t_0}{\omega} < \sum_{\beta} v_{s \beta}(\omega) \).

Thus the second factor on the right hand side cf. eq. (34) is smaller than
\[
1 + \sum_{\beta} v_{s \beta}(\omega) + \sum_{\beta, \gamma} v_{s \beta}(\omega) v_{s \gamma}(\omega) + \cdots
\]
when \( \omega < E_B^F \).

In order to write the above expression, we have used the following identity :
\[
\left( \sum_{\beta} v_{s \beta}(\omega) \right)^2 = \sum_{\beta} v_{s \beta}(\omega) v_{s \beta}(\omega) = \sum_{\beta} v_{s \beta}(\omega) \sum_{\gamma} v_{s \gamma}(\omega) = \sum_{\beta} v_{s \beta}(\omega) v_{s \beta}(\omega)
\]
indeed, we know that
\[
\sum_{\gamma} v_{s \gamma}(\omega) = \sum_{\beta} v_{s \beta}(\omega).
\]

The expression above converges absolutely for \( \omega < E_B^F \) since it is inferior to a geometric series
\[
1 + x + x^2 \text{ with } x = \sum_{\beta} v_{s \beta}(\omega) < 1.
\]

Thus the second factor on the right hand side of eq. (34) is positive and finite for \( \omega < E_B^F \). Because of (24") the first factor is non vanishing for \( \omega < E_B^F \). Thus \( \omega + t_0 - \Sigma_{\beta}(\omega) \neq 0 \) for \( \omega < E_B^F \). This means that the ground state energy should be \( E_B^F \) i.e. the energy of the completely aligned ferromagnetic state. Is there another eigenstate with energy \( E_B^F \) and with a spin \( S < S_{\text{max}} \)? In order to answer this question, let us first examine the wave function of the completely ferromagnetic state. Setting
\[
\psi_{IF} = C_{i_1}^+ C_{i_2}^+ \cdots C_{i_1}^- C_{i_2}^- \cdots C_{i_N}^+ | 0 >
\]
the wave function of the completely ferromagnetic state corresponding to energy \( E_B^F \) is
\[
\psi_F = \sum_{\ell} \gamma_{\ell} \psi_{IF}
\]
and satisfies the equation
\[
\left\{ t \sum_{\mu} C_{i\mu}^* C_{i\sigma} + t_0 (n_{01} + n_{01} - 1) \right\} \sum_{\ell} \gamma_{\ell} \psi_{IF} =
E_B^F \sum_{\ell} \gamma_{\ell} \psi_{IF}
\]
whence \( \gamma_1 \) satisfies the equation
\[
\gamma_1 (E_B^F + t_0 \delta_{10}) = -t \sum_{i=m(j)} \gamma_1.
\]

It is straightforward to show that there is only one solution for this set of homogeneous linear equation such that \( \gamma_1 \) tends to zero as \( i \) goes to infinity. Let us now consider a wave function \( \psi \) of the state with energy \( E_B^F \) and arbitrarily given \( N_1 \) and \( N_0 \), and let us expand it with \( \psi_{IF} \), as
\[
\psi = \sum_{i} \Gamma_{i} \psi_{IF}.
\]

Then from
\[
H^* \psi = E_B^F \psi
\]
we get the equation for \( \Gamma_{i} \) :
\[
\Gamma_{i} = \gamma_{i}.
\]

Nagaoka showed that in the two and the three dimensional case all lattice points \( i_2 \) in the superlattice are connected directly or indirectly. In that case it is clear that a solution for eq. (37) is provided by the solution of eq. (35) namely
\[
\Gamma_{i} = \gamma_{i},
\]
independent of \( \beta_j \).

The wave function (36) with \( \Gamma_{i} \) determined by eq. (38) and eq. (35) is obtained from
\[
\psi_F = \sum_{i} \gamma_{i} \psi_{IF}
\]
by applying \( (S_-) \) \( N \) times. Therefore it corresponds to
\[
S = S_{\text{max}} \text{ and } S_z = \frac{(N_1 - N_0)}{2}.
\]

The solution defined by eq. (38) is unique, as can be shown by subtracting from eq. (37) another hypothetical solution and showing that such a solution must differ from the eq. (38) by a constant which is necessarily zero in order to satisfy the boundary conditions.

4.4 PHYSICAL MEANING OF THE GROUND STATE THEOREM FOR THE LOCALIZED STATE CASE. — Let us first notice that only loops contribute to \( v_{s \beta}(\omega) \), since retraceable paths do not change the spin configuration. Thus all retraceable paths are contained in \( v_{s}(\omega) \), which may also contain the contribution from closed loops.

A term such as
\[
\left( \frac{\omega}{\omega + t_0} \right) v_{s \beta}(\omega) v_{s \beta}(\omega)
\]
is the contribution from all paths starting from the origin with spin configuration $\gamma$, returning once to the origin after having changed the spin configuration $\beta$, leaving the origin again and returning a second time to the origin after having restored the original spin configuration $\alpha$. For example, in the Antiferromagnetic spin configuration, letting $\alpha$ correspond to the configuration, $1a$, $\beta$ to $1b$ and $\gamma$ to $1c$ one sees easily that $\Sigma_0(\omega)$ contains a term proportional to $(\omega + \omega + t_0)$ from a fourth order term in $v_{\beta\alpha}(\omega)$ and another fourth order term in $v_{\gamma\alpha}(\omega)$ resulting from a clockwise motion of the hole around the loop, followed by a counter clockwise motion to return back to the original spin configuration. The next terms proportional to $(\omega + \omega + t_0)$ are at least of order 10 in $t/\omega$. Thus the lowest order term in $(t/\omega)$ in $\Sigma_0(\omega)$ proportional to $(\omega + \omega + t_0)$ is an 8th order term. Similarly, it is easy to check that the lowest order term proportional to $(\omega + \omega + t_0)^2$ arises from the lowest order term in $v_{\beta\alpha}(\omega) v_{\beta\gamma}(\omega) v_{\gamma\alpha}(\omega)$ and is proportional to $(t/\omega)^2$.

Looking at eq. (34), one sees readily that one regains the ferromagnetic configuration self energy by setting all non diagonal $v_{\beta\alpha}(\omega)$ equal to zero. Indeed, in the ferromagnetic configuration, all paths returning to the origin are diagonal in spin configuration. Thus the second bracket on the right of eq. (34) describes the modification to the self energy which arises from the suppression of some closed loops in $\Sigma_0(\omega)$ as a result of spin disorder. For example, consider the change in $\Sigma_0(\omega)$ to lowest order in $(\omega + \omega + t_0)$, i.e. to 0th order. We find

$$
\Sigma_0(\omega) = \Sigma_0^{F}(\omega) - \omega \sum_{\beta \neq \alpha} v_{\beta\alpha}(\omega)
= \Sigma_0^{F}(\omega) - \left( \omega \sum_{\beta \neq \alpha} v_{\beta\alpha}(\omega) - \omega v_{\alpha\alpha}(\omega) \right)
= \omega v_{\alpha\alpha}(\omega).
$$

To lowest order in $t/\omega$, the change in $\Sigma_0(\omega)$ is thus given by the smallest closed loop such that the original spin configuration is not restored after the hole has completed the path back to the origin. One may approximately evaluate the change in energy of the bound state by flipping a single spin somewhere in the lattice in an otherwise fully ferromagnetic crystal. In order to find the exact change in energy one would have to solve exactly for the zeroes of the second factor on the right of eq. (34).

Let the flipped spin first be nearest neighbour to the impurity center. The change $\delta \Sigma$ in the self energy is given by the smallest closed loop of figure 1a, the contribution of which is $\omega(t/\omega)^2$. Since, in a cubic lattice there are 4 such loops, we have

$$
\delta \Sigma = 2.4 \omega \left( \frac{t}{\omega} \right)^2.
\tag{39}
$$

The factor 2 arises from the different ways of walking along the path, clockwise or anticlockwise.

An approximate expression for the change in the bound state energy is obtained by replacing $\omega$ in eq. (39) by $E_B^F$. One obtains thus

$$
\delta E_B \approx 8 | E_B | \left( \frac{t}{ E_B } \right)^4.
\tag{40}
$$

It is necessary to check whether this approximate solution is not drastically in error because of higher order terms in $(\omega + \omega + t_0)$, or because of other larger closed loops which are suppressed by the flipped spin.

To 0th order in $(\omega + t_0)$, the change in $\delta E_B$ is minimized by eq. (39) since one neglects larger closed loops, or decorated closed loops such as shown on figure 6. Each correction is of order

$$
\left( \frac{t}{ E_B } \right)^2 = \frac{1}{z^2} \left( \frac{zt}{ E_B } \right)^2 < z^{-2}.
\tag{41}
$$

There are in 3 dimensions 14 possible ways of inserting vertex corrections similar to figure 6c and 10.5 different ways of placing a closed loop such as 6d on the lattice (avoiding double counting). Thus the corrections we consider may be as large as

$$
\frac{49}{2z^2} \left( \frac{zt}{ E_B } \right)^2.
$$

If the bound state is far below the band edge, i.e. $|zt/E_B| \ll 1$ the correction is small. But if the bound state sits just below the band edge, i.e. if $|zt/E_B| \ll 1$, then for three dimensions and $z = 6$, the value for $\delta E_B$ in eq. (39) is about 70 % too small. One could improve the approximation by renormalizing the closed loop of figure 6a by all insertions of the type 6b and 6c of all orders which pass the flipped spin and do not retrace the first step before passing the flipped spin. This is done in Appendix II and yields an important renormalization of the correction (39) when

$$
E_B^F \sim |zt|.
$$

---

**Fig. 6.** a) F configuration with one flipped spin nearest neighbour to the impurity, b) smallest suppressed closed loop, c) suppressed « decorated » closed loop, d) larger suppressed closed loop.
Let us now examine corrections which arise from terms of order one in \((\omega/\omega + t_0)\). Such corrections arise to higher order in \(t/\omega\) than the previous ones, and are opposite in sign: indeed, for each closed loop suppressed by a spin flip another closed loop appears in the self energy: that obtained by retracing the suppressed one to regain the original spin configuration. Thus the bare correction (39) should be replaced by

\[
\delta \Sigma' = 8 \left| \frac{t}{\omega} \right|^3 \left( 1 - \frac{\omega}{\omega + t_0} \left( \frac{t}{\omega} \right)^4 \right). \tag{42}
\]

We have for the eigenstate \(\omega_B\)

\[
\omega_B + t_0 = \Sigma_0(\omega_B)
\]

whence

\[
|\omega_B + t_0| > z \left| \frac{t^2}{\omega_B} \right|.
\]

Thus the correction in eq. (42) is

\[
\frac{\omega_B}{\omega_B + t_0} \left( \frac{t}{\omega_B} \right)^4 < \frac{1}{z^3} \left( \frac{zt}{\omega_B} \right)^2.
\]

Thus even when \(E_B^F \sim zt\), the corrections arising from the non-diagonal paths are at least \(6^3 = 216\) times smaller than the main term in three dimensions, and 64 times smaller in two dimensions.

Thus the approximate change in the bound state energy from its value for the fully ferromagnetic state to the value with one spin flip at a site nearest neighbour to the impurity is of the order of

\[
8 \frac{zt}{z^2} \left| \frac{zt}{E_B^F} \right|^3 \sim 3 \times 10^{-3} (2zt) \tag{43}
\]

for \(zt/E_B^F \leq 1\).

\[
\sim 0.6 \times 10^{-2} \text{ eV} \quad \text{if} \quad 2zt = 2 \text{ eV}
\]

for \(zt/E_B^F \leq 1\).

For 2 dimensions, with \(z = 4\), we may have

\[
\delta E_B \gtrsim \frac{2}{(4)^3} \left| \frac{zt}{E_B^F} \right|^3 2zt \tag{44}
\]

\[
\gtrsim 8 \times 10^{-3} (2zt)
\]

if \(2zt = 1.33\) eV (i.e. \(t\) unchanged compared with the 3 dimensional example above)

\[
\delta E_B \gtrsim 1.1 \times 10^{-2} \text{ eV}.
\]

Expressions (43) and (44) exhibit a noticeable ferromagnetic coupling between spins nearest neighbour to the impurity. This effect is largest when the bound hole sits nearest to the band edge, so that its spatial extension is largest. The coupling decreases as \((zt/E_B^F)^3\) as \(E_B^F\) sinks away from the band edge. This effect is a kind of excluded volume effect: a spin flip increases the kinetic energy of the bound hole because the number of paths available for diagonal propagation decreases. This effect is directly connected to the band narrowing effect described by Brinkman and Rice in the pure case when the spin configuration becomes antiferromagnetic or random.

One may derive an approximate expression for the change in the bound state energy when the flipped spin is far away from the impurity center. Let the distance to the flipped spin be \(R = qa_0\) where \(a_0\) is the lattice spacing.

Then the smallest suppressed closed loop has a length \(L \sim 2qa_0 + 2a_0\).

Thus the change in the self energy is

\[
\delta E_B(R) \sim E_B z^{-2(R/a_0 + 1)} \left( - \frac{zt}{E_B} \right)^{2(R/a_0 + 1)} \tag{45}
\]

whence, when \(E_B \sim zt\)

\[
\delta E_B(R) \sim \frac{z}{z^2} \exp \left( - \frac{R}{a_0} \ln z \right) \tag{45'}
\]

where \(z \sim z\) is the number of suppressed loops of length \(L\) which pass the flipped spin. Thus the ferromagnetic coupling which stabilizes the ferromagnetic ground state is in fact exponentially decreasing with distance, and is negligible beyond nearest neighbours.

Until now we have considered the case of an impurity localized just below the band edge. It is straightforward to show that for a more attractive potential, such that \(z \sim 1\) the ferromagnetic stabilization of spins around the localized hole is much less effective. This is quite clear on eq. (40), or on eq. (45). The coupling to a distant site becomes:

\[
\delta E_B(R) \approx \frac{z}{z^2} \exp \left( - \frac{R}{a_0} \ln z \right) \times \exp \left( - \frac{2}{a_0} \ln \left| \frac{E_B}{zt} \right| \right). \tag{46}
\]

Remarks:

1) Although the band edge moves away faster from the impurity level than the latter moves up, since \(E_B^F < -zt\), the level may be in the exponential tail region [4]. We ignore this complication here.

2) The exponential damping of the ferromagnetic coupling with distance is an illustration of a theorem due to Izuyama, who showed that the spin wave energy is zero in complete ferromagnetism for our Hamiltonian [18].

4.5 Displacement of the Bound State from the AF Configuration to the R Configuration.

Let \(\omega_B^R\) be the energy of the bound state when the spin configuration is antiferromagnetic. When the spin configuration changes to a random one, the main change comes from the opening of the smallest
closed loop, the spin weight of which goes from zero (AF configuration) to \( \frac{1}{2} \) for the random spin configuration. Thus the bound state energy is lowered from \( \omega_B^{AF} \) to \( \omega_B^R \). We can estimate the change

\[
\delta \omega_B = | \omega_B^R - \omega_B^{AF} |
\]

as was done before in the F case to estimate the strength of the ferromagnetic coupling

\[
\delta \omega_B \simeq \frac{1}{4} \cdot \left( \frac{2 \times 4}{z^4} \right) \left( \frac{-z t}{\omega_B^{AF}} \right)^4 | \omega_B^{AF} | \tag{47}
\]

equation (47) is just equation (39) with a factor \( \frac{1}{2} \) to account for the probability that three random spins are aligned.

Taking \( \omega_B^{AF} \simeq 0.4 z t \), we obtain

\[
\delta \omega_B \simeq 3 \times 10^{-3} z t.
\]

An important difference arises in this case with the displacement studied in the previous section; in the present case, the band edge may now catch up with the bound state, if \( t_0 > t_0 > t_0^{AF} \). The reason is that the change in the band edge is proportional to \( (zt/W_{AF})^3 \) rather than \( (zt/\omega_B^{AF})^3 \) and

\[
| W_{AF} | < | \omega_B^{AF} |.
\]

4.6 SMALL IMPURITY POTENTIAL. — For \( t_0 < t_0^{AF} \), the impurity potential is not large enough to localize a state, whatever the spin configuration.

The theorem on the ground state still holds in that case, as can be inferred from equation (29) to (34). In the ferromagnetic configuration, the eigenstates are scattered Bloch states, given by the standard Slater-Koster impurity treatment. In a different spin configuration, the impurity Green’s function is obtained from equation (32) or (34). The impurity contribution to the density of state in the random configuration is given approximately, using the Retraceable Path Approximation by

\[
\frac{1}{\pi} \text{Im} \Sigma_{B}(\omega + i \eta) \left( \frac{\omega + t_0 + \text{Re} \Sigma_{B}(\omega)}{2} + (\text{Im} \Sigma_{B}(\omega)) \right)^2 \tag{48}
\]

where \( \Sigma_{B}(\omega) \) is given by equation (14).

It is clear that the perturbed density of states is quite different in the R case than in the F case for the same potential. An example is shown on figure 7 for the two spin configurations when \( t_0 \) is just below the critical value \( t_0^{AF} \) necessary to bind a state in the R configuration.

4.7 EFFECT OF A MAGNETIC FIELD. — Let us now investigate the effect of a magnetic field on the system, when the spin configuration is R in zero field.

The probability for a closed loop of \( n \) steps to be open for the hole propagation is

\[
(1 + \exp 2 x)^{-n-1} + (1 + \exp(-2 x))^{-n-1}
\]

Fig. 7. — Perturbed density of states for \( t_0 < t^R \), a) R configuration (Retraceable Path Approximation), b) F configuration.

\[ x = \beta \mu_B H. \]

Thus if \( \omega_B^R \) is the bound state energy in zero field in a R configuration, the approximate expression for the energy lowering due to an external field is, to 3rd order in \( (t/\omega) \):

\[
\delta \omega_B^R(H) = \{(1 + \exp 2 x)^{-3} + \}
\]

\[
+ (1 + \exp(-2 x))^{-3} \} \frac{8}{z^4} \left( \frac{zt}{\omega_B^R} \right)^3 z t. \tag{49}
\]

Thus for low fields, i.e. \( x \ll 1 \)

\[
\delta \omega_B^R(H) = \frac{1}{4} \left( 1 + 3 \left( \frac{\mu_B H}{k_B T} \right)^2 \right) \frac{8}{z^4} \left( \frac{zt}{\omega_B^R} \right)^3 z t. \tag{50}
\]

For high fields, i.e. for \( x \gg 1 \)

\[
\delta \omega_B^R(H) = (1 - 3 e^{-2 x}) \frac{8}{z^4} \left( \frac{zt}{\omega_B^R} \right)^3 z t. \tag{51}
\]

The bound state moves all the way from \( \omega_B^R(H = 0) \) to \( \omega_B^R(H) \), i.e. the energy of the bound state for a fully aligned F configuration in the presence of an external field \( H \). Equation (51) is only approximate, since it describes only the result of opening completely the smallest closed loop for hole propagation, while
all closed loops are available for hole propagation with spin factor 1 in the limit of high fields.

4.8 INSULATOR METAL TRANSITION UNDER THE EFFECT OF A MAGNETIC FIELD. — If the impurity potential \( t_0 \) is larger than \( t_0^F \), the bound state remains bound whatever the spin configuration.

— If the impurity potential \( t_0 \) is smaller than \( t_0^F \), the impurity cannot bind a state, whatever the spin configuration.

— But if \( t_0^{AF} < t_0 < t_0^F \), then various situations may arise:

a) if \( t_0^{AF} < t_0 < t_0^R \), the state which was bound in the AF configuration will collapse in the R band upon going from AF to R,

b) if \( t_0^R < t_0 < t_0^F \), the state which was bound in the R configuration may collapse in the F band, or in the partially ordered band, for the value of the magnetic field such that the band edge coincides with the bound state since the mobility becomes infinite for the completely ferromagnetic state, a metallic state is reached if the concentration of impurities is large enough (\( C \sim 10^{-4} \)). A similar effect may arise in the absence of an external field, as a result of the temperature dependent variation of the magnetization in a ferromagnet, when the polarization is large enough for the band edge to coincide with the bound state. As a first approximation, if \( \langle S_z \rangle \) is the average ferromagnetic spin polarization per site, the spin factor for a closed loop of \( n \) steps is

\[
(P_+)^{n-1} + (P_-)^{n-1}
\]

with \( P_\pm = \frac{1}{2} \pm \langle S_z \rangle \).

For example, the displacement of the bound state from above \( \langle S_z \rangle \) to a temperature \( \langle S_z \rangle \), is to third order in \( t/\omega \) :

\[
\delta \omega H(T) = \left\{ \left( \frac{1}{2} + \langle S_z(T) \rangle \right)^3 + \left( \frac{1}{2} - \langle S_z(T) \rangle \right)^3 \right\} \frac{8}{z^4} \left( \frac{zt}{\omega H(T)} \right)^3 zt
\]  

(52)

when the polarization is small, i.e. \( \langle S_z(T) \rangle \ll 1 \)

\[
\delta \omega H(T) = \frac{1}{4} (1 + 24 \langle S_z(T) \rangle^2) \frac{8}{z^4} \left( \frac{zt}{\omega H(T)} \right)^3 zt
\]  

(53)

when the polarization is large, i.e.

\[
\frac{1}{2} - \langle S_z(T) \rangle \ll 1 .
\]

Then

\[
\delta \omega H(T) \approx \left( 1 - 3 \left( \frac{1}{2} - \langle S_z(T) \rangle \right) \right) \frac{8}{z^4} \left( \frac{zt}{\omega H(T)} \right)^3 zt .
\]

(53’)

As for eq. (51), eq. (53’) is only qualitative, in that it neglects the change in \( \delta \omega H(T) \) due to all closed loops being available for propagation in this limit.

Eq. (52) and (53) rely on a molecular field approximation and on the neglect of short range correlations between neighbouring spins, which arise as a result of a coupling \( \sim t^2/U \) when \( U \) is finite. Short range correlations between spins occur in the problem for the calculation of the spin factors for a given closed loop. This problem is dealt with in reference [10].

4.9 TRANSPORT PROPERTIES. — 4.9.1 Magneto-resistance. — Ohata and Kubo [13] computed the high temperature magnetoresistance in the pure system by taking into account the change in the spin factors of closed loops upon applying an external magnetic field. For small magnetic fields they find

\[
\sigma = \frac{N_b}{\Omega} e \mu
\]

with

\[
\mu \approx \frac{2 e \sqrt{\pi}}{k_B T} \approx a^2 \left( 1 + \left( \frac{\mu_B H}{k_B T} \right)^2 \right) + \cdots
\]

(54)

where \( a \) is the interatomic distance.

For large magnetic fields,

\[
\mu = \frac{e}{k_B T} \sqrt{\frac{8}{6 \pi}} a^2 \exp \left( 2 \frac{\mu_B H}{k_B T} \right).
\]

(55)

Eq. (54) agrees nicely with the result obtained by Brinkman and Rice [4] for zero field in the Retraceable Path Approximation. They found that the mobility was approximately given by

\[
\mu = 2 \beta a^2 t^2 \int_{-z t}^{z t} \frac{d \omega}{\pi} e^{-\beta \omega (|\text{Im} G(\omega - i \eta)|)^2}
\]

\[
\int_{-z t}^{z t} \frac{d \omega}{\pi} e^{-\beta \omega (|\text{Im} G(\omega' - i \eta)|)}
\]

(56)

The mobility is thus proportional to the average over the thermally occupied states of the hopping probability \( z t^2 |\text{Im} G(\omega - i \eta)| \). The \( \text{Im} G(\omega - i \eta) \) simply measures the density of states at the neighbouring site.

The low mobility obtained (\( \mu \sim 70 \text{cm}^2/\text{V.s} \) for \( \beta z t = 100 \) and \( a = 3 \text{A} \)) reflects the fact that the hole essentially undergoes Brownian motion through the lattice when the spin configuration is random.

Eq. (55), on the other hand, yields an infinite mobility for the hole in infinite field as expected for a ferromagnetic alignment of spins.

Ohata and Kubo have also studied the effect on transport properties of a random distribution of donor atoms [11]. In their scheme, when the spins are almost perfectly ordered, the effect of lattice randomness is simply to give an additional contribution to the value of the resistivity, while it is smeared out when the spins are nearly completely disordered.

However they have considered donor atoms as weak scatterers, and they have not considered the
possibility for donor atoms to bind the hole at low temperatures. If the scattering potential is large enough to bind a state in a given spin configuration, the resistivity for zero field is

$$\sigma \sim \frac{1}{\Omega} \exp \frac{E_b}{k_B T} \epsilon \mu$$  \hspace{1cm} (57)$$

where $\mu$ is approximately given by eq. (56). We have shown [10] that in the presence of a magnetic field, eq. (57) becomes

$$\sigma(H) \sim \frac{1}{\Omega} \exp \frac{E_b(H)}{k_B T} \epsilon \mu(H)$$  \hspace{1cm} (58)$$

where $\mu(H)$ is given by eq. (54) and (55) and

$$E_b(H) = \begin{cases} E_b(0) - 0.4 \left( \frac{\mu_b H}{k_B T} \right)^2 z \tau & \text{for low fields} \\ E_b(0) - \alpha \exp - 2 \left( \frac{\mu_b H}{k_B T} \right) z \tau & \text{for high fields} \end{cases}$$  \hspace{1cm} (59)$$

The main variation of the excitation energy with the field is due to the band edge shift, as computed in reference [10] and not to the bound state shift, which is roughly smaller by a factor $(\epsilon z / \omega_b)^2 z^{-3}$.

If the bound state is sufficiently near the band edge for zero field, i.e. for example if $t_0 > T_0 > t_b$, the magnetic field effect may be dramatic, since the activation energy may go to zero for sufficiently strong field. In that case there is a giant negative magnetoresistance. Eq. (59) exhibits an interesting feature: the measurement of the magnetoresistance allows for a determination of the band width $2 z \tau$.

When the impurity potential is much larger than $t_b$, i.e. when the bound state is deep and strongly localized on the impurity center, the magnetic field effect is less dramatic. However the excitation energy varies like the band edge with the magnetic field, as in eq. (59). The maximum variation is

$$E_b(\infty) - E_b(0) \sim 0.20 z \tau,$$

which can be of the order of 0.2 eV for a band width of the order of 2 eV.

4.9.2 Temperature dependence of the activation energy below $T_c$. — Large effects on the activation energy are expected to occur as a result of the temperature-dependent spin configuration. Here again, in the activation energy, the largest changes upon spin ordering are due to the band edge shifts with spin ordering.

Within the molecular field approximation, and if one neglects short range correlations and retains only the long range order, the calculation is similar to that of the magnetoresistance, and is based on the approximate expression for the probability for a spin to be aligned in the positive or the negative $z$ direction, if the long range spin polarization is $\langle S_z \rangle$. We have simply, as before $P_{z} = \frac{1}{2} \pm \langle S_z(T) \rangle$. Then we have, as discussed by us in reference [10]:

$$\sigma(T) = \frac{1}{\Omega} \exp \frac{E_b(T)}{k_B T} \epsilon \mu(T)$$

with

$$E_b(T) \approx \begin{cases} E_b(T_0) - 0.4 \langle S_z \rangle^2 z \tau & \text{for } \left| \frac{T - T_c}{T_c} \right| \ll 1 \\ E_b(0) - \alpha \exp - 2 \langle S_z \rangle & \text{for low } T. \end{cases}$$

We discuss in greater detail the situation when short range order is taken into account in reference [10].

5. Comments and experimental discussion. —

5.1. Comments. — In the theory developed in this paper, we have used a crude model for the magnetic insulator:

1) We have neglected corrections of order $t/U$, which, as shown by Harris and Lange [19], lead to terms in the Hamiltonian of the form

$$\sum_{i,j=1} C_{i,j}^{\alpha} (1 - n_{i,j}) C_{-i,-j}^{\alpha} + \frac{2 \sqrt{t_i^2}}{U} \left( S_\alpha S_\beta - \frac{1}{2} \rho_\alpha \rho_\beta \right)$$

where

$$S_\alpha = \frac{1}{2} \sum_{i,j} C_{i,j}^{\alpha} C_{i,j}^{\alpha^*} \sigma_{\alpha\beta^*},$$

$$\rho_\alpha = \sum_{\sigma} C_{i,j}^{\alpha} C_{i,j}^{\alpha}$$

Brinkman and Rice [4] have discussed the effect of these corrections on the parameters of the pure system, and they showed that the bulk of the band density of states is little affected while the tails, which reach out to the full band width when $U = 0$, may be significantly reduced.

In our case it is obvious that the ferromagnetic configuration which is stabilized around the impurity when $U = 0$ will be destroyed by the exchange interactions as soon as $t_i^2 / U \sim \Delta E_b$. However the coupling between spins nearest neighbour to the impurity is changed by the presence of the bound hole. A detailed study of this effect for finite $U$ will appear elsewhere [10], as well as the effect on the hole activation energy. However for temperatures significantly larger than the ordering temperature, our results for the magnetoresistance for example, are essentially valid.

2) We have also neglected orbital degeneracy and intra-atomic exchange, which produces a large additional narrowing of the AF density of states (50%) and of the R density of states (35%). In the dilute impurity problem which we have studied here, this results in an increased stabilization of the ferromagnetic configuration around the bound hole, as well as in a larger magnetic field effect in the magnetoresistance [10].
We should emphasize that all the many body aspects of the problem we have treated are contained in the spin configuration factors which are attached to closed loops in the various spin configurations, and which produce the changes in the impurity self-energy when the spin configuration changes.

5.2 Comparison with experiment. — The theory described in this paper applies particularly to insulating transition metal oxides, many of which are magnetic. As far back as 1936, Verwey and De Boer [20] recognized that in those compounds, 3d electrons are localized at the metal ions. According to these authors, a necessary condition for an appreciable conductivity in these oxides is the presence of ions of the same element with different valency at crystallographically equivalent lattice points. In NiO, for example, this can be achieved by creating Ni vacancies or more easily by substituting Li for Ni at Ni sites. Each Li$^+$ ion is then compensated by a Ni$^{3+}$ ion. At low temperatures the holes formed by the Ni$^{3+}$ are bound to the effectively negative Li$^+$ ions. At high temperatures, the holes are free and can move through the lattice by the interchange of electrons between Ni$^{3+}$ and Ni$^{2+}$ ions. There has been considerable discussion, in the literature, after numerous studies, to determine whether an activation energy was needed in this transfer process, and whether the activation energy occurring in the conductivity was the energy needed for loosening the holes from the Li$^+$ ions, or due to a thermally activated hopping [20] to [27]. However, measurements of the Hall effect [22], [25] of the Seebeck coefficient and conductivity [26]-[27] show that the mobility is not activated, and that the activation energy is indeed connected with the loosening of the hole from the Li$^+$ ion. Several authors [27]-[28] have argued that the low mobilities imply small polaron formation. However the calculations of Ohata and Kubo, and of Brinkman and Rice, have ignored all ionic effects, and therefore all possible polaron effects, while they yield values of the mobility close to those seen experimentally in a material such as NiO.

Two different excitation energies have been observed [29] below $T_N$ and above $T_N$ in Li$_x$Ni$_{1-x}$O. The excitation energy $\varepsilon_2 \sim 0.30$ eV below $T_N$ is larger than $\varepsilon_1 \sim 0.15$ eV above $T_N$. It is however not possible to determine whether this is due to the shift of the band edge from AF to R configuration, for two reasons: a) we have not studied carefully enough the effect of finite exchange integrals $t_r^2/U$ and b) within the model employed in our study, there is very little shift in the band edge for NiO upon spin disordering, because NiO is in fact a planar antiferromagnet. The density of states for a PAF (Planar AntiFerromagnetic) configuration has been shown to be very similar to that of a R configuration [30]. It is however quite possible that orbital degeneracy removes this similarity in a PAF and that the difference $\varepsilon_2 - \varepsilon_1$ is due to the shift of the band edge. We have not yet investigated the effect of orbital degeneracy and intra-atomic exchange on the density of states.

As of now, we do not know of any clear-cut observation of the change in excitation energy for a bound hole in a doped magnetic insulator upon spin disordering. We believe that experimental studies on doped magnetic insulators are of interest, especially as the change in excitation energy is directly related to the band width.

As for the magnetoresistance, there is experimental evidence for the negative magnetoresistance computed by Ohata and Kubo [13] in Sb-doped Ge [31]. This system is a narrow band with random atomic positions, and is not directly related to the dilute alloy we have studied here. Experimental studies of magnetoresistance in dilute alloys of the type Li$_x$Ni$_{1-x}$O with low ordering temperatures and with different spin orderings are of interest.

It should be pointed out that the ferromagnetic insulator EuO exhibits impurity effects which are quite analogous to the effects we describe in this paper although a completely different theory applies in this case. The conductivity of EuO may increase by many orders of magnitude as the temperature is decreased below the ferromagnetic ordering temperature [32] to [35]. The conductivity above 50 K is thermally activated with an activation energy which depends linearly in the long-range magnetic order [3]. Below 50 K the conductivity is metallic. This insulator metal transition is observed only in sample which are slightly oxygen deficient, presumably in the form of vacancies. There is a red shift in the optical absorption edge, by several tenths of an eV to lower energy with decreasing temperature. The magnetococonductivity in the neighbourhood of $T_c$ is very large, the ratio $\sigma(H = 20$ kOe)/$\sigma(0)$ at $T_c$ being about 10$^6$.

The model we have discussed here does not apply to EuO, and one cannot understand the properties of this system of an extra electron propagating in a 4f-level. Instead, one must include the shift of the conduction band which is polarized by exchange interactions with the localized 4f electrons and introduce impurity levels connected with non stoechiometry. The detailed mechanism for the insulator metal transition in EuO is still unclear [36]-[37].

APPENDIX I

We have neglected in part 4 any change in overlap integral between the impurity cell wave function and the nearest neighbours.

It is possible to extend the previous discussions to the case where impurity-host and host transfer integrals $t_{AB}$ and $t_{BB}$ are different.
Brouers et al. [38] have derived a generalization of the Koster Slater formula for random transfer integrals. The change in the site diagonal Green's function is given by the following expression

$$\Delta G_{00}(z) = -\delta_0 \frac{\partial G_{00}(z)}{\partial z} - \frac{G_{00}(z) + z}{G_{00}(z) - \delta_0^2 (zG_{00}(z) - 1)}$$

(A.1)

with

$$\delta_0 = \varepsilon_A - \varepsilon_B$$

and

$$\delta_1 = \frac{t_{AB}}{t_{BB}}$$

The function $G_{00}(z)$ is the pure host site diagonal Green's function. The expression above is identical to the usual Slater Koster formula when $\delta_1 = 1$. The impurity levels are given by the poles of $A$, and are localized if these poles are located on the real axis. One can see by considering the solutions of

$$(z - \delta_0) G_{00}(z) - \delta_1^2 (zG_{00}(z) - 1) = 0$$

that the plane $\delta_0 - \delta_1$ is divided in three regions corresponding to zero, one or two localized impurity states. The curves delimiting these regions are simply given by the parabola

$$\delta_0 = \pm \omega_0 - t_{AB}(\pm \omega_0 - G_{00}^{-1}(\pm \omega_0))$$

where $\pm \omega_0$ are the limits of the host-band.

For a ferromagnetic insulator:

$$\delta_0 = \pm 1 - t_{AB}(\pm 1 - G_{00}^{-1}(\pm 1))$$

and

$$G_{00}(\pm 1) \simeq \pm 1.477.$$  

In the Rice Brinkman Retraceable Path Approximation for the R-configuration

$$\delta_0 = \pm 0.745 - t_{AB}(\pm 0.745 - G_{00}^{-1}(\pm 0.745))$$

with

$$G_{00}(\pm 0.745) \simeq \pm 3.34.$$

The results are summarized on figure 8.

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**APPENDIX II**

In this appendix, we study the renormalized contribution of the closed loops associated with the smallest suppressed closed loop shown in figure 6b when one spin is flipped at one of the nearest neighbours of the impurity.

Doniach, Fisher and Roulet [30] have discussed the renormalization procedure for a number of paths in the magnetic insulator problem. We use their notation. $R_l(z)$ is the generating function for paths which do not pass the origin more than once in the F configuration $R_l(z) = \sum p A_p z^p$, where $A_p$ is the number of paths of $p$ steps. $R(z)$ is the generating function for paths which pass the origin any number of times. $R_{ij}(z)$ is the generating function for a path which goes from $i$ to $j$, without restriction. We call $iR_{ij}(z)$ a path from $i$ to $j$ which does not pass the site $l$ on the way. $q$ is the coordination number.

Then, the generating function for the renormalized path $0 \rightarrow 1 \rightarrow 2 \rightarrow 3 \rightarrow 0$ is the product of:

1) The generating function for paths going from 0 to 1, i.e.

$$q R_{01}(z) = \frac{1}{q^z} R_1(z).$$

2) The generating function for paths going from 1 to 2 without passing 0 on the way, i.e.

$$q R_{12}(z) = \frac{1}{q^z} \left( R_1(z) - \frac{1}{q} R_1(z) \right).$$

3) The generating function for paths going from 2 to 3 without passing 0 or 2 on the way

$$q R_{23}(z) = \frac{1}{q^z} R_1(z) - (q R_{20}(z) R_2(z)).$$

We have approximately:

$$q R_{20} \simeq \frac{1}{q(q - 1)} R_1(z) \left( 1 - \frac{1}{q(q - 1)} \right).$$
and
\[ 2R_{03} = R_{03} - (2R_{02})(R_{23}) \]
\[ = \frac{R(z)}{q^2} - \frac{R_1(z)}{q^2(q(q-1)-1)} \]
whence
\[ 0.2R_{23}(z) = \frac{1}{q^2} R_1(z) - \frac{R_1(z)}{q^2(q(q-1)-1)} R(z) \left( \frac{R(z)}{q^2(q(q-1)-1)} \right) \]

4) The generating function for paths going from 3 to 0 without passing through 2 on the way
\[ zR_{30} = qR_{30} - (0.2R_{32})(0.2R_{20}) \]
We find
\[ qR_{30} = \frac{1}{q^2} \frac{R_1(z)}{R(z)} \left( 1 - \frac{R_1(z)}{q} \right) \]
and
\[ 0.2R_{32} = zR_{32} - (0.2R_{30})(zR_{02}) \]
where we used \[ 3R_{32} = 2R_{32} - 0.2R_{30} \].
We have
\[ zR_{0.2} = 0R_{20} = \frac{1}{q(q-1)} \frac{R_1(z)}{R(z)} \left( 1 - \frac{1}{q(q-1)} \right) \]
and
\[ zR_{32} = \frac{1}{q^2} R_1(z) \]
\[ 0.2R_{32} = \frac{R_1(z)}{q^2} R(z) \left( 1 - \frac{1}{q(q-1)} \right) \]
whence
\[ zR_{30} = \frac{R_1(z)}{q^2} R(z) \left( 1 - \frac{1}{q(q-1)} \right) \]
References
[17] This theorem can be proved following the proof of the Nagaoka theorem given by LIEB, E. in the Proceedings of the XIVth Solvay Conference.