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Effective Exchange Interactions for Magnetic Surfaces, Overlayers and Surface Impurities in the Itinerant Model of Ferromagnetism

by

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ABSTRACT

Many studies of 'surface' properties of transition metals have been made in the past few years. These surface properties are determined by the local band structure which is directly related to the magnetization density. It is well known that long-wavelength spin-waves exist in any ferromagnet, in particular in an Itinerant one and they determine the magnetization at low temperatures. The general aim of this thesis is to investigate the behaviour of spin-waves on the surface of an Itinerant ferromagnet while it may be covered with an overlayer of impurities or with isolated impurities. The spin-wave energies in metallic ferromagnets are determined by the Transverse Dynamical susceptibility of the system. It is shown that the static unenhanced susceptiblity of an Itinerant ferromagnet can be interpreted as an effective exchange interaction of the type obtained for a Heisenberg ferromagnet. This is the basis of our work which is then used in the physical interpretation of properties of surface spin-waves in transition metals. In the first part of the thesis, the mapping of the spin-wave problem for a semi-infinite metallic ferromagnet (modelled by a simple cubic tight-binding crystal) on an equivalent problem for an insulator is discussed. The effect of surface is treated as a perturbation to the bulk problem. Both the Bulk spin-wave Green's function and the surface perturbation are parametrized in terms of Heisenberg-like effective exchange integrals. This formulation is exact in the Random Phase Approximation (RPA) for long-wavelength spin-waves. The effect of surface is separated into the 'geometric' effect (ie cutting all the bulk effective exchange integrals across the surface) and a surface renormalization of the bulk exchange integrals (due to surface core-shift, HF corrections and Friedel oscillations). The main part of the thesis is concerned with a generalization of this model to impurities embedded in the surface and to impurities above the surface. The general theory obtained is then applied to an Fe impurity on a Pd substrate, and it is shown that the system can become unstable for certain critical values of its parameters.

Chapter 1 Itinerant Model of Ferromagnetism.

1.1 Introduction 1

The ferromagnetism of transition metals of the iron group has been interpreted by various models which are classified essentially into two groups. The first is the 'localized spin model' which is based on the atomic or Heitler-London theory, where it is assumed that the magnetic electrons are localized on each atom in the crystal. The second is the 'itinerant-electron model' which is based on the molecular orbital or energy-based theory, where it is assumed that the magnetic electrons are band electrons which travel through the crystal as running waves.

Each of these approaches has its advantages and disadvantages, but in certain physical situations, one approach may be more appropriate than the other. The 'itinerant-electron model' is the appropriate model for the description of electron transport and specific heat in the metals, while the 'localized-spin model' is the appropriate one for the description of exciton states in an ionic crystal. It is found experimentally that the d-electrons of transition metals have properties characteristic of both the 'itinerant-electron model' and the 'localised-spin model'. The experimental agreement on the non-half integral atomic moments are explained directly in terms of the 'itinerant-electron model', while the strong temperature dependence of the susceptibilities of transition metals are more conveniently discussed in terms of the localized spins.

However a type of theory capable of reconciling these two models for a ferromagnetic metal such as Fe has been derived. (See J Hubbard; 1979).

The spin-wave state is one in which the motion of the spin density at one point in space is correlated with that at another point, (Bloch; 1932). It is these correlated effects in narrow bands which lead to the atomic behaviour and it is only by taking correlation effects into account that one can understand how d-electrons exhibit both kinds of behaviour simultaneously. (See J Hubbard; 1963)

1.2 An Approximate Representation of Exchange Interaction in Transition Metals.

In this section, the approximate model of electron interactions in narrow energy bands used in later calculations is described. Although our assumption is such that ferromagnetism of itinerant electrons is possible only for a degenerate band and not for a single band, we take in the following, the advantage of simplification by considering an s-band. However, we shall assume we are dealing with 3d-transition metal electrons.

Consider a hypothetical partly-filled narrow s-band, containing n electrons per atom. The Bloch functions $\Psi_{n\underline{k}}$[(n = 1, ...,5) for the d-band] are assumed to have been calculated in some appropriate Hartree-Fock potential. The ferromagnetic transition metal is characterized by means of the one-band Hubbard Hamiltonian. (See J Hubbard ; 1963):

$$H = \sum_{\underline{k},\sigma} E_{\underline{k}}\, n_{\underline{k}\sigma} + U \sum_{i,\sigma} n_{i\sigma}\, n_{i,-\sigma} \qquad (1.2.1)$$

where $\underline{k}$ is the wave-vector ; σ is the spin index ; $\bar{\sigma}$ indicates spin opposite to σ ; $E_{\underline{k}}$ is the energy corresponding to $\Psi_{\underline{k}}$; $n_{\underline{k}\sigma}$ and $n_{i\sigma}$ are the occupation numbers in the Bloch and Wannier representations respectively. They are defined by

$$\begin{aligned} n_{\underline{k}\sigma} &= c^{\star}_{\underline{k}\sigma}\, c_{\underline{k}\sigma} \\ n_{i\sigma} &= c^{\star}_{i\sigma}\, c_{i\sigma} \end{aligned} \qquad (1.2.2)$$

The operators $c^*_{\underline{k}\sigma}$, $c_{\underline{k}\sigma}$ and $c^*_{i\sigma}$, $c_{i\sigma}$ are the creation and destruction operators of electron in the Bloch and Wannier representations respectively, related by

$$c^*_{i\sigma} = \frac{1}{\sqrt{N}} \sum_{\underline{k}} e^{-i\underline{k}.\underline{R}_i} c^*_{\underline{k}\sigma}$$

(1.2.3)

$$c_{i\sigma} = \frac{1}{\sqrt{N}} \sum_{\underline{k}} e^{i\underline{k}.\underline{R}_i} c_{\underline{k}\sigma}$$

U is the Coulomb repulsion when two electrons are situated on the same atomic site.

More generally,

$U_{m\underline{k},n\underline{k}'}$ is of the form:

$$U_{m\underline{k},n\underline{k}'} = \iint \Psi^*_{m\underline{k}}(\underline{r}_1)\, \Psi^*_{n\underline{k}'}(\underline{r}_2)\, V(\underline{r}_1-\underline{r}_2)\, \Psi_{m\underline{k}}(\underline{r}_2)\, \Psi_{n\underline{k}'}(\underline{r}_1) d\underline{r}_1 d\underline{r}_2$$

(1.2.4)

where $V(\underline{r}_1-\underline{r}_2)$ is the Coulomb interaction ; $V(\underline{r}_1-\underline{r}_2) = \frac{e^2}{\underline{r}_{12}}$ within a unit cell.

We define the Wannier function $a_n(\underline{r}-\underline{R}_i)$ by

$$\Psi_{n\underline{k}}(\underline{r}) = \frac{1}{\sqrt{N}} \sum_{\underline{R}_i} e^{i\underline{k}.\underline{R}_i} a_n(\underline{r}-\underline{R}_i) \qquad (1.2.5)$$

The interaction (1.2.4) involves two integrals:

(i) U_n – the intra-atomic Coulomb integral,

$$U_n = \iint |a_n(\underline{r}_1)|^2 \frac{e^2}{\underline{r}_{12}} |a_n(\underline{r}_2)|^2 \, d\underline{r}_1 \, d\underline{r}_2 \qquad (1.2.6)$$

(ii) J_{mn} – the intra-atomic exchange integral of Hund's rule type,

$$J_{mn} = \iint a_m^*(\underline{r}_1) \, a_n^*(\underline{r}_2) \frac{e^2}{\underline{r}_{12}} a_m(\underline{r}_2) \, a_n(\underline{r}_1) \, d\underline{r}_1 \, d\underline{r}_2 \qquad (1.2.7)$$

and also has important integrals involving nearest neighbouring interactions.

For the sake of comparison, one may note that $U \sim 20$ eV for 3d-electrons in transition metals.

The largest of the neglected terms in Eq (1.2.4) are those of nearest neighbours which can be estimated to have the order of magnitude ~ 2 eV. (See N F Mott; 1964).

For Nickel with 0.6 holes (magnetic carriers) per atom, the Hund's rule J_{mn} plays a small role since two holes rarely come on the same atom due to correlation effects not included in the Hartree-Fock approximation. On the other hand, J_{mn} is significant in Iron and Cobalt. (See E P Wolfarth ; 1980).

One may use Hartree-Fock (HF) and Random Phase Approximation (RPA) replacing U with U^{eff} which takes into account the correlation effects. In the case of the Hamiltonian of Eq (1.2.1), this amounts to simply replacing the term

$\sum_{i,\sigma} n_{i\sigma} n_{i,-\sigma}$ by $\sum_{i,\sigma} n_{i\sigma} \langle n_{i,-\sigma} \rangle$ for all i, and this gives the energy

$$E_{HF} = \sum_{\underline{k}} \sum_{\sigma} E_{\underline{k}} \, n_{\underline{k}\sigma} + U^{eff} \sum_{\sigma} n_{\sigma} n_{-\sigma} \qquad (1.2.8)$$

where n_σ is the number of particles with spin σ, per atom at any site i.

We can write

$$Un_\sigma \, n_{-\sigma} = \tfrac{1}{4} U[(n_\sigma + n_{-\sigma})^2 - (n_\sigma - n_{-\sigma})^2] \qquad (1.2.9)$$

Then

$$Un_\sigma \, n_{-\sigma} = -\tfrac{1}{4} U(n_\sigma - n_{-\sigma})^2 + \text{constant} \qquad (1.2.10)$$

(See E D Thompson ; 1963)

Eq (1.2.10) can be written in terms of the relative magnetization ζ, where

$$\zeta = \frac{n_\sigma - n_{-\sigma}}{n} \tag{1.2.11}$$

and $n = n_\sigma + n_{-\sigma}$; giving

$$Un_\sigma \underline{n}_\sigma = -\tfrac{1}{4} U \zeta^2 n^2 + \text{constant} \tag{1.2.12}$$

Eq (1.2.12) is in fact the expression for the additional energy of the system arising from the magnetization of the solid in the 'Stoner' model (1938, 1946). Thompson, Wolfarth and Bryan (1964) showed that

$$n_\sigma = \begin{cases} \frac{n}{2}(1+\zeta) & \text{for} \quad \sigma = \uparrow \\ \frac{n}{2}(1-\zeta) & \text{for} \quad \sigma = \downarrow \end{cases}$$

$$= \int_0^\infty N(E) \quad f^\sigma(E) \quad dE. \tag{1.2.13}$$

where

$$f^{\sigma}(E) = \frac{1}{1 + e^{(E-\mu^{\sigma})/k_B T}} \quad . \qquad \text{for} \quad \sigma = \uparrow, \downarrow \qquad (1.2.14)$$

is the 'Fermi-Dirac function' for σ-spin particles, μ^{σ} is the corresponding chemical potential often called the Fermi-level ; $k_B = 1.38062$ the Boltzmann constant ; T is the temperature and N(E) is the density of states.

The total energy (the sum of the one-particle energies) in the 'Stoner model', is given by

$$E = \sum_{\underline{k},\sigma} E_{\underline{k}} \, n_{\underline{k}\sigma} - \tfrac{1}{4} U \zeta^2 n^2. \qquad (1.2.15)$$

At T = 0, Eq (1.2.15) is equivalent to

$$E = \int_0^{E_F^{\sigma}} E \, N(E) \; dE + \int_0^{E_F^{-\sigma}} E \, N(E) \; dE \; - \tfrac{1}{4} U \zeta^2 n^2. \qquad (1.2.16)$$

with

$$n_{\sigma} = \int_0^{E_F^{\sigma}} N(E) \; dE. \qquad \text{for} \quad \sigma = \uparrow, \downarrow \qquad (1.2.17)$$

where E_F^{σ} is the Fermi-level in σ-spin band.

The criterion for ferromagnetism is obtained by comparing the energy E given by Eq (1.2.15) for small ζ at $T = 0$, with the paramagnetic energy E_o. It is found (See E D Thompson, E P Wolfarth and A C Bryan ; 1964) that

$$E = E_o + \frac{n^2 \zeta^2}{4 N(E_F)} - \frac{1}{4} U n^2 \zeta^2 \qquad (1.2.18)$$

where $N(E_F)$ is the density of states per atom at the Fermi-level.

Eq (1.2.18) can be written in the form

$$E = E_o + \frac{n^2 \zeta^2}{4 N(E_F)}[1 - U N(E_F)] \qquad (1.2.19)$$

From Eq (1.2.19) , it is clear that the energy is less on magnetizing ; if

$$U N(E_F) > 1. \qquad (1.2.20)$$

Thus, if for any E_F the condition (1.2.20) satisfied, then the system will become ferromagnetic.

1.3 Green's Functions and Resolvents.

The application of Green's functions is widespread in 'solid-state theory' and in the theory of 'many-particle systems'. The importance of Green's functions in solid state physics arises from the fact that exact expressions for many physical properties such as density of states and susceptibility may be written in terms of them. Also, the poles of a Green's function determine the excitation energies of a system.

We shall here give a brief discussion on some properties of the Green's function. However, the reader is referred to Zubarev (1960) for a detailed account.

1.3.1 The Retarded Green's Function

There are three kinds of Green's Functions, namely the Causal G_c the Advanced $G^{(-)}$ and the Retarded $G^{(+)}$.

$$G_c(t,t') = \langle\langle A(t) \,;\, B(t') \rangle\rangle_c$$

$$= -i \langle T\, A(t)\, B(t') \rangle \qquad (1.3.1)$$

$$G^{(-)}(t,t') = \langle\langle A(t) \,;\, B(t') \rangle\rangle^{(-)}$$

$$= i\, \theta(t' - t) \langle [A(t), B(t')] \rangle \qquad (1.3.2)$$

$$G^{(+)}(t,t') = \langle\langle A(t) \,;\, B(t') \rangle\rangle^{(+)}$$

$$= -i\, \theta(t - t') \langle [A(t), B(t')] \rangle \qquad (1.3.3)$$

$\langle\langle A(t) \,;\, B(t') \rangle\rangle$ is an abbreviated notation for a Green's function. $\theta(t)$ is the Heaviside step-funciton defined by

$$\theta(t) = \begin{cases} 1 & t > 0 \\ 0 & t < 0 \end{cases} \qquad (1.3.4)$$

$\langle \ldots \rangle$ indicates averaging over a grand canonical ensemble defined by

$$\langle \ldots \rangle = Q^{-1} \, \mathrm{Tr} \, (e^{-\frac{\mathcal{H}}{k_B T}}) \tag{1.3.6}$$

$\mathcal{H}$ is an operator defined by

$$\mathcal{H} = H - \mu N \tag{1.3.7}$$

where H is the time-independent Hamiltonian operator ; μ is the chemical potential often called the Fermi-level and N is the total number of particles.

$A(t)$ and $B(t')$ are the Heisenberg representations of the operators A and B expressed by

$$A(t) = e^{i\mathcal{H}t} \, A(0) \, e^{-i\mathcal{H}t} \tag{1.3.8}$$

The symbol T in the Causal Green's function is the time ordering operator which is defined by

$$T \, A(t) \, B(t') = \begin{cases} A(t) \, B(t') & t > t' \\ \eta \, B(t') \, A(t) & t < t' \end{cases} \tag{1.3.9}$$

$\eta = \pm 1.$

The sign of η is chosen positive or negative by considering what is most convenient for the problem. One usually chooses the positive sign if A and B are Bose operators, and the negative sign if they are Fermi operators. The choice of operators A and B is determined by the condition of the problem.

[A,B] indicates the commutator or the anti-commutator:

$$[A,B] = AB - \eta\, BA. \tag{1.3.10}$$

Since $\langle\langle A(t) ; B(t') \rangle\rangle^{(\pm)}$ are functions of (t − t') only, one can define for real E, the Fourier transforms

$$\langle\langle A ; B \rangle\rangle_E^{(\pm)} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle\langle A(t) ; B(t') \rangle\rangle^{(\pm)} e^{iEt}\, dt \tag{1.3.11}$$

1.3.2 Equation of Motion For The Green's Function $G(t,t')$.

The operators A and B satisfy an equation of motion of the form

$$i\frac{dA}{dt} = [A, H] \qquad (1.3.12)$$

where H is the time-independent Hamiltonian.

Thus, the operators $\langle\langle A(t) ; B(t') \rangle\rangle^{(\pm)}$ given by Eqs (1.3.2) and (1.3.3) can be differentiated w.r.t t in this fashion, ie

$$i\frac{d G^{(\pm)}(t,t')}{dt} = i \frac{d}{dt} \langle\langle A(t) ; B(t') \rangle\rangle^{(\pm)}$$

$$= \frac{d\theta(t-t')}{dt} \langle [A(t), B(t')] \rangle +$$

$$\langle\langle [A(t), H] ; B(t') \rangle\rangle^{(\pm)} \qquad (1.3.13)$$

Using the relationship between the discontinuous function $\theta(t)$ and the δ-function of t, ie

$$\delta(t) = \frac{d\theta(t)}{dt} \qquad (1.3.14)$$

we can write

$$i \frac{d}{dt} \langle\langle A(t) ; B(t') \rangle\rangle^{(\pm)} = \delta(t-t') \langle [A(t), B(t')] \rangle + \langle\langle [A(t), H] ; B(t') \rangle\rangle^{(\pm)} \qquad (1.3.15)$$

The second-term in the R.H.S of Eq (1.3.15) shows a chain of Green's functions which are simply equations of motion and must be supplemented by boundary conditions. The nature of these boundary conditions shall be discussed in the next section.

1.3.3 Spectral Representations.

In this section, we shall derive the spectral representations for the time correlation functions $\langle A(t)\ B(t') \rangle$ and $\langle B(t')\ A(t) \rangle$. These functions are the averages over the statistical ensemble of the product of operators A and B in Heisenberg representation. It is important to have these representations since they supplement the set of equations of motion for Green's functions (See Eq 1.3.15) with the necessary boundary equations.

Let $|n\rangle$ be the eigenfunction of the operator $\mathcal{H}$ given by Eq (1.3.7) and E_n its corresponding eigenvalue. We can now write

$$|n\rangle = E_n |n\rangle. \qquad (1.3.16)$$

Then using Eq (1.3.5), the time correlation function $\langle A(t)\ B(t') \rangle$ can be written in the form

$$\begin{aligned}\langle A(t)\ B(t') \rangle &= Q^{-1}\ \mathrm{Tr}(e^{-\frac{\mathcal{H}}{\theta}}\ A(t)\ B(t')) \\ &= Q^{-1} \sum_n \langle n| e^{-\frac{\mathcal{H}}{\theta}}\ A(t)\ B(t') |n\rangle \\ &= Q^{-1} \sum_n \langle n| A(t)\ B(t') |n\rangle\ e^{-\frac{E_n}{\theta}} \qquad (1.3.17)\end{aligned}$$

where $\theta = k_B T$.

Using the completeness relation, ie

$$\sum_m |m\rangle\langle m| = 1 \qquad (1.3.18)$$

in Eq (1.3.17), we obtain

$$\langle A(t)\,B(t')\rangle = Q^{-1} \sum_{n,m} \langle n|A(t)|m\rangle\langle m|B(t')|n\rangle\, e^{-\frac{E_n}{\theta}} \qquad (1.3.19)$$

Using Eq (1.3.8) for both operators A(t) and B(t'), we have

$$\begin{aligned} A(t) &= e^{i\mathcal{H}t}\, A(0)\, e^{-i\mathcal{H}t} \\ B(t') &= e^{i\mathcal{H}t'}\, B(0)\, e^{-i\mathcal{H}t'} \end{aligned} \qquad (1.3.20)$$

where

$$\begin{aligned} e^{-i\mathcal{H}t}|n\rangle &= e^{-iE_nt}|n\rangle \\ \langle m|e^{i\mathcal{H}t} &= \langle m|e^{iE_mt} \end{aligned} \qquad (1.3.21)$$

Substituting Eqs (1.3.20) and (1.3.21) into Eq (1.3.19), we obtain

$$\langle A(t)\, B(t') \rangle = Q^{-1} \sum_{m,n} A_{nm} B_{mn}\, e^{-\frac{E_n}{\Theta}}\, e^{i\omega_{mn}(t'-t)} \qquad (1.3.22)$$

where

$$A_{nm} = \langle n \backslash A(0) \backslash m \rangle$$

$$B_{mn} = \langle m \backslash B(0) \backslash n \rangle \qquad (1.3.23)$$

$$\omega_{mn} = E_m - E_n$$

Similarly, we have

$$\langle B(t')\, A(t) \rangle = Q^{-1} \sum_{n,m} B_{nm} A_{mn}\, e^{-\frac{E_n}{\Theta}}\, e^{i\omega_{mn}(t-t')} \qquad (1.3.24)$$

By interchanging the summation indices m and n, Eq (1.3.22) becomes

$$\langle A(t)\, B(t') \rangle = Q^{-1} \sum_{m,n} A_{mn} B_{nm}\, e^{-\frac{E_m}{\Theta}}\, e^{i\omega_{mn}(t'-t)} \qquad (1.3.25)$$

Fourier transforming both Eqs (1.3.24) and (1.3.25), we have

$$\langle B(t')\, A(t) \rangle = \int_{-\infty}^{\infty} \phi(\Omega)\, e^{-i\Omega(t-t')}\, d\Omega \qquad (1.3.26)$$

and

$$\langle A(t)\, B(t') \rangle = \int_{-\infty}^{\infty} \phi(\Omega)\, e^{\frac{\Omega}{\theta}}\, e^{-i\Omega(t - t')}\, d\Omega \qquad (1.3.27)$$

where we have introduced the notation

$$\phi(\Omega) = Q^{-1} \sum_{m,n} A_{mn}\, B_{nm}\, e^{-\frac{E_m}{\theta}}\, \delta(\omega_{mn} - \Omega) \qquad (1.3.28)$$

Eqs (1.3.26) and (1.3.27) are the required spectral representations for the time correlation functions and $\phi(\Omega)$ is the spectral intensity of $\langle B(0)\, A(t) \rangle$.

Using the commutation eq (1.3.10), the Retarded Green's function $G^{(+)}$ of Eq (1.3.3) can be written in the form

$$\begin{aligned} G^{(+)}(t,t') &= -i\theta(t - t') \langle A(t)\, B(t') + B(t')\, A(t) \rangle \\ &= -i\theta(t - t') \{ \langle A(t)\, B(t') \rangle + \langle B(t')\, A(t) \rangle \} \end{aligned} \qquad (1.3.29)$$

Fourier transforming Eq (1.3.29), we have

$$G^{(+)}(E) = \langle\langle A;B \rangle\rangle_E^{(+)} = \int_{-\infty}^{\infty} -i\theta(t) \{ \langle A(t)\, B(0) \rangle + \langle B(0)\, A(t) \rangle \}\, e^{iEt}\, dt \qquad (1.3.30)$$

Now, using Eqs (1.3.27) and (1.3.28) in Eq (1.3.30), we have

$$G^{(+)}(E) = -i \int_{-\infty}^{\infty} d\Omega \, \phi(\Omega)(e^{\Omega/\Theta} + 1) \int_{-\infty}^{\infty} dt \, e^{i(E - \Omega)t} \, \Theta(t) \qquad (1.3.31)$$

where by the definition of $\Theta(t)$ we can write

$$\int_{-\infty}^{\infty} dt \, e^{i(E - \Omega)t} \, \Theta(t) = \frac{i}{E - \Omega + i\epsilon} \qquad (1.3.32)$$

which when substituted in Eq (1.3.31), yields

$$G^{(+)}(E) = \int_{-\infty}^{\infty} \phi(\Omega) \, (e^{\Omega/\Theta} + 1) \frac{d\Omega}{E - \Omega + i\epsilon} \qquad (1.3.33)$$

and similarly, the advanced Green's function can be written in the form

$$G^{(-)}(E) = \int_{-\infty}^{\infty} \phi(\Omega) \, (e^{\Omega/\Theta} + 1) \frac{d\Omega}{E - \Omega - i\epsilon} \qquad (1.3.34)$$

If E is now taken to be complex, then $G^{(\pm)}(E)$ can be continued analytically in the complex E plane. In the case of $G^{(+)}(E)$, the integral (1.3.11) converges provided $\text{Im}\, E > 0$, so $G^{(+)}$ can be defined and is a regular function of E in the upper half of the complex E - plane. This can be written mathematically in the form of

$$G(E) = \begin{cases} G^{(+)}(E) & \text{for} \quad \mathrm{Im}\, E > 0 \\ G^{(-)}(E) & \text{for} \quad \mathrm{Im}\, E < 0 \end{cases} \qquad (1.3.35)$$

ie G(E) is an analytic function throughout the whole complex E-plane except on the real axis.

Interchanging E and Ω in both Eqs (1.3.33) and (1.3.34) and then subtracting them, we get

$$G^{(+)}(\Omega + i\epsilon) - G^{(-)}(\Omega - i\epsilon) =$$

$$= \int_{-\infty}^{\infty} \phi(E)\, (e^{\frac{E}{\Theta}} + 1) \left[\frac{1}{\Omega - E + i\epsilon} - \frac{1}{\Omega - E - i\epsilon}\right] dE \qquad (1.3.36)$$

Using the δ-function representation, ie

$$\delta(x) = \frac{1}{2\pi i} \left[\frac{1}{x - i\epsilon} - \frac{1}{x + i\epsilon}\right] \qquad (1.3.37)$$

We arrive at

$$G^{(+)} - G^{(-)} = -2\pi i \int_{-\infty}^{\infty} \phi(E)\, (e^{\frac{E}{\Theta}} + 1)\, \delta(\Omega - E)\, dE \qquad (1.3.38)$$

The difference between the two Green's functions can also be written in terms of $\text{Im}\, G^{(+)}$, ie

$$G^{(+)} - G^{(-)} = 2i \; \text{Im}\, G^{(+)} \tag{1.3.39}$$

(Since $G^{(+)}$, $G^{(-)}$ are complex conjugates of one another.)

By using Eqs (1.2.38) and (1.3.39) , we can now obtain the spectral intensity, ie

$$\phi(\Omega) = -\frac{1}{\pi} \frac{\text{Im}\, G^{(+)}(\Omega)}{e^{\frac{\Omega}{\Theta}} + 1} \tag{1.3.40}$$

Now that $\phi(\Omega)$ is determined, the spectral representation for the correlation function given by Eq (1.3.27) can be written as

$$\langle B(t')\, A(t) \rangle = -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\text{Im}\, G^{(+)}(\Omega)}{e^{\frac{\Omega}{\Theta}} + 1} \; e^{-i\Omega(t - t')} \; d\Omega \tag{1.3.41}$$

By setting $t' = 0$, and

$$f(\Omega) = \frac{1}{e^{\frac{\Omega}{\Theta}} + 1} \tag{1.3.42}$$

Eq (1.3.41) can be transformed to

$$\langle B(0)\, A(t) \rangle = -\frac{1}{\pi} \int_{-\infty}^{\infty} \mathrm{Im}\, G^{(+)}(\Omega)\, f(\Omega)\, e^{-i\Omega t}\, d\Omega \qquad (1.3.43)$$

1.3.4 The Density of States

For the time-independent Schrödinger operator (E–H) we can expand in terms of the eigenfunctions of H, provided that zero is not an eigenvalue of H. (See Landsberg 1969). Then

$$G = (E - H)^{-1} \, |n\rangle\langle n|$$

$$= \sum_n \frac{|n\rangle\langle n|}{E - E_n} \qquad (1.3.44)$$

where $|n\rangle$ satisfies

$$(E - H)\,|n\rangle = 0 \qquad (1.3.45)$$

We can now define the Green's operators $G^{(\pm)}$ by the equation

$$G^{(\pm)}(E) = \frac{1}{E - H \pm i\epsilon} \qquad (1.3.46)$$

$$= \sum_n \frac{|n\rangle\langle n|}{E - E_n \pm i\epsilon}$$

Using the following definitions for the delta function and the principal value respectively

$$\delta(x) = \frac{1}{\pi} \lim_{\epsilon \to 0} \frac{\epsilon}{x^2 + \epsilon^2} \tag{1.3.47}$$

$$P(x) = \frac{x}{x^2 + \epsilon^2} \tag{1.3.48}$$

We obtain

$$G^{(\pm)}(E) = \sum_n \left| n \right\rangle\left\langle n \right| [P(E - E_n) \mp i\,\pi\,\delta(E - E_n)] \tag{1.3.49}$$

Then

$$G^{(+)}(E) - G^{(-)}(E) = -\,2\pi i \sum_n \left| n \right\rangle\left\langle n \right| \delta(E - E_n) \tag{1.3.50}$$

Now consider Eq (1.3.50) in an arbitrary representation $\left| 1 \right\rangle$. Then

$$\left\langle 1 \right| G^{(+)} - G^{(-)} \left| 1' \right\rangle = -\,2\pi i \sum_n \left\langle 1 | n \right\rangle\left\langle n | 1' \right\rangle \delta(E - E_n) \tag{1.3.51}$$

The diagonal elements in Eq (1.3.51) are

$$\langle 1 \backslash G^{(+)} - G^{(-)} \backslash 1 \rangle = -2\pi i \sum_n \langle 1 \backslash n \rangle\langle n \backslash 1 \rangle \, \delta(E - E_n) \tag{1.3.52}$$

Summing over all the states 1 and interchanging the order of summation on the R.H.S of Eq (1.3.52), we have

$$\sum_1 \langle 1 \backslash G^{(+)} - G^{(-)} \backslash 1 \rangle = -2\pi i \sum_n \sum_1 \langle 1 \backslash n \rangle\langle n \backslash 1 \rangle \, \delta(E - E_n)$$

$$= -2\pi i \sum_n \delta(E - E_n) \tag{1.3.53}$$

For a system with a continuous spectrum, $\sum_n \delta(E - E_n)$ is the sum of a large number of energy levels in the neighbourhood of E. The number of such levels per unit energy interval dE is defined to be the density of states $\rho(E)$. Since the two functions $G^{(+)}$ and $G^{(-)}$ are complex conjugates, we have from Eqs (1.3.39) and (1.3.53),

$$-2\,\pi i\,\rho(E) = 2i \sum_1 \text{Im}\, G^{(+)}_{11}(E).$$

$$\text{ie} \quad \rho(E) = -\frac{1}{\pi} \sum_1 \text{Im}\, G^{(+)}_{11}(E). \tag{1.3.54}$$

$$= -\frac{1}{\pi}\, \text{Tr}(\, \text{Im}\, G^{(+)}) \tag{1.3.55}$$

The density of states per atom, where N is the number of particles in the system is then given by

$$\rho^{(n)}(E) = \frac{1}{N}\rho(E). \tag{1.3.56}$$

1.3.5 The One-Particle Green's Function For The Hubbard Model With HF Approximation.

To discuss the conditions under which a local moment may form and to compute the magnitude of the moment, one customarily studies the one-particle Green's function $G^{\sigma,\sigma'}(\underline{k}_1, \underline{k}_2; t)$, which gives information about a system of electrons, ie one-particle excitation. The Retarded one-particle Green's function is defined as follows:

$$G^{\sigma,\sigma'}(\underline{k}_1, \underline{k}_2; t) = \langle\langle c_{\underline{k}_1\sigma}(t) \,;\, c^{*}_{\underline{k}_2\sigma'} \rangle\rangle$$

$$= -i\Theta(t) \langle [c_{\underline{k}_1\sigma}(t) \,,\, c^{*}_{\underline{k}_2\sigma'}(0)] \rangle \tag{1.3.57}$$

Where $c_{\underline{k}\sigma}$ and $c^{*}_{\underline{k}\sigma}$ are the destruction and creation operators of electrons in the Bloch representation respectively. These operators are anitcommutating, ie

$$[c_{\underline{k}_1\sigma} \,,\, c^{*}_{\underline{k}_2\sigma'}] = c_{\underline{k}_1\sigma}\, c^{*}_{\underline{k}_2\sigma'} + c^{*}_{\underline{k}_2\sigma'}\, c_{\underline{k}_1\sigma} \tag{1.3.58}$$

$$= \delta_{\underline{k}_1\underline{k}_2}\, \delta_{\sigma\sigma'}$$

In the Wannier representation, the one-particle Green's function $G^{\sigma,\sigma'}$ becomes

$$G^{\sigma,\sigma'}_{ij}(t) = \langle\langle c_{i\sigma}(t) \, ; \, c^{*}_{j\sigma'}(0) \rangle\rangle$$

$$= - i\theta(t) \langle [c_{i\sigma}(t) \, , \, c^{*}_{j\sigma'}(0)] \rangle \qquad (1.3.59)$$

Where $c_{i\sigma}$ and $c^{*}_{i\sigma}$ are the destruction and creation operators of electrons at the site $\underline{R}_i$, in the Wannier representation. These operators are given in terms of $c_{\underline{k}\sigma}$ and $c^{*}_{\underline{k}\sigma}$ by Eq (1.2.3), for an infinite sample.

The Green's function $G^{\sigma\sigma}$ of the Hartree-Fock Hubbard Hamiltonian given by Eq (1.2.1) is usually referred to as the HF one-electron Green's function.(We shall require this function in later section.) For example, the poles of the RPA dynamic susceptibility discussed in Sec 2.3 (which give spin-wave energies) can always be expressed in terms of these functions. Therefore a brief discussion is included here.

In an operator form, the HF one-electron Green's function is given by

$$G^{\sigma}_{ij}(t) = \langle\langle c_{i\sigma}(t) \, , \, c^{*}_{j\sigma}(0) \rangle\rangle$$

$$= -i\theta(t) \langle [c_{i\sigma}(t) \, , \, c^{*}_{j\sigma}(0)] \rangle \qquad (1.3.60)$$

(For simplicity, we have chosen to write $G^{\sigma\sigma}$ as G^{σ}.)

G^{σ} is a diagonal matrix in the Bloch-representation, whose elements are given by

$$G^{\sigma}(\underline{k},\underline{k}) = \frac{1}{E^{\sigma} - E_{\underline{k}} + i\delta} \qquad (1.3.61)$$

where

$$E^{\sigma} = \begin{cases} E & \text{for } \sigma = \uparrow \\ E-\Delta & \text{for } \sigma = \downarrow \end{cases} \qquad (1.3.62)$$

Δ is the exchange splitting.

In the Wannier representation, G^{σ} becomes

$$G^{\sigma}_{ij} = \frac{1}{N} \sum_{\underline{k}} \frac{e^{i\underline{k}.\underline{R}}}{E^{\sigma} - E_{\underline{k}} + i\delta} \qquad (1.3.63)$$

where $R = \underline{R}_i - \underline{R}_j$.

Chapter 2 Spin-Wave Green's Functions of the Heisenberg and Itinerant Ferromagnets.

2.1 Introduction 2.

Consider a spin with spin quantum number S and Z-component of angular momentum S_i^z ($\hbar = 1$), localized at each lattice site in a ferromagnet. A spin-wave is a 'sinusoidal disturbance' of such spins. (Sinusoidal disturbance describes a quantity which changes in magnitude with time according to a sine curve).

It was first shown by Bloch that states near the ground-state of a ferromagnet (where it is generally assumed that all spins are lined up) can be approximated by superposition of these sinusoidal spin-waves.

This was discussed on the basis of the Heisenberg model for magnetic insulators, with Hamiltonian

$$H^o = -\sum_{l,l'} J_{ll'} \underline{S}_l \cdot \underline{S}_{l'} \qquad (2.1.1)$$

where the summation is taken over all combinations of nearest-neighbour spins $\underline{S}_l$ and $\underline{S}_{l'}$, and $J_{ll'}$ is the exchange integral between nearest-neighbour spins.

We now define two new operators S_l^+ and S_l^- for spin

$\underline{s}_l = (s^x, s^y, s^z)$ such that

$$s_l^+ = s_l^x + i\, s_l^y$$

$$s_l^- = s_l^x - i\, s_l^y \qquad (2.1.2)$$

The operator s_l^+ corresponds to the removal of a particle of ↓-spin and replaces it by a particle of ↑-spin ; the operator s_l^- has the opposite effect. These operators are called spin-deviation operators.

Substituting Eqs (2.1.2) into Eq (2.1.1) , we obtain

$$H^o = - \sum_{l,l'} J_{ll'} \left[\tfrac{1}{2} (s_l^+ s_{l'}^- + s_{l'}^- s_l^+) + s_l^z s_{l'}^z\right] \qquad (2.1.3)$$

We now make a further approximation and replace the spin-deviation operators by the spin-raising and lowering operators c_l^* and c_l respectively , ie

$$s_l^+ = c_l^*$$

$$s_l^- = c_l \qquad (2.1.4)$$

$(s = \tfrac{1}{2})$

where c_l^* and c_l obey the Bose commutation rules:

$$[c_l, c_{l'}^*] = c_l c_{l'}^* - c_{l'}^* c_l = \delta_{ll'}$$

$$[c_l, c_{l'}] = [c_l^*, c_{l'}^*] = 0 \,. \tag{2.1.5}$$

so that s_l^z becomes

$$s_l^z = \tfrac{1}{2} - c_l^* c_l \,. \tag{2.1.6}$$

Using c_l^* and c_l in the Bloch-representation, ie

$$c_l^* = \frac{1}{\sqrt{N}} \sum_{\underline{q}} c_{\underline{q}}^* e^{i\underline{q}.\underline{l}}$$

$$c_l = \frac{1}{\sqrt{N}} \sum_{\underline{q}} c_{\underline{q}} e^{-i\underline{q}.\underline{l}} \tag{2.1.7}$$

Our Hamiltonian of Eq (2.3) becomes

$$H^o = \sum_{\underline{q}} \left\{ \sum_{\underline{R}} J(\underline{R}) \left(1 - e^{-i\underline{q}.\underline{R}}\right) \right\} c_{\underline{q}}^* c_{\underline{q}} \tag{2.1.8}$$

where $\underline{R} = \underline{R}_l - \underline{R}_{l'}$ $\qquad l \neq l'$

(See J M Ziman ; 1972).

If we denote the ground-state of a ferromagnet by $\psi_{\underline{o}}$, then an excited state with one particular spin reversed, is given by

$$\psi_{\underline{q}} = \frac{1}{N} \sum_{l} e^{i\underline{q}.\underline{R}_l} \; S_l^- \; \psi_{\underline{o}} \tag{2.1.9}$$

Using the Hamiltonian (2.1.8), the spin-wave energy $E_{\underline{q}}$ of such a state is then given by

$$E_{\underline{q}} = \hbar\omega_{\underline{q}} = \sum_{\underline{R}} J(\underline{R}) \, (1 - e^{-i\underline{q}.\underline{R}}) \tag{2.1.10}$$

For a simple cubic lattice with only nearest neighbour interaction and $\underline{q}.\,\underline{R} \ll 1$, Eq (2.1.10) becomes

$$E_{\underline{q}} = \hbar \, \omega_{\underline{q}} = 6 \, J \, a^2 \, q^2 \tag{2.1.11}$$

where $\omega_{\underline{q}}$ is the frequency of the assumed wave-vector $\underline{q}$, a is the lattice constant and $J = J(\underline{R})$ is taken to be a constant for any nearest neighbour exchange.

2.2 Bulk Spin-Wave Green's Function of The Heisenberg Ferromagnet.

In this section, we shall determine the matrix elements of the Green's function $1/(E - H^{o})$, where H^{o} is given by Eq (2.1.1)

Our model is an infinite simple cubic crystal with lattice constant a, such that the lattice sites are given by the translation vectors $\underline{x}_l$ defined by

$$\underline{x}_l = l_1 \underline{a}_1 + l_2 \underline{a}_2 + l_3 \underline{a}_3 \tag{2.2.1}$$

where

$$\underline{a}_1 = (1\ 0\ 0)$$

$$\underline{a}_2 = (0\ 1\ 0) \tag{2.2.2}$$

$$\underline{a}_3 = (0\ 0\ 1)$$

and l_1, l_2, l_3 are three integers which can be positive, negative or zero ; and to which we refer collectively as l.

We now introduce a real, symmetric $(N \times N)$ matrix D^{o}, whose elements are

$$D^{o}_{ll'} = J_{ll'} \qquad l' \neq l. \qquad (2.2.3)$$

$$D^{o}_{ll} = - \sum_{l'} J_{ll'} \qquad (2.2.4)$$

$(l' \neq l)$

Eq (2.1.3) can now be written as

$$H^{o} = \sum_{l,l'} D^{o}_{ll'} \, c^{*}_{l} \, c_{l'} \qquad (2.2.5)$$

Here, it is interesting to note that by the definition of the transverse susceptibility of the Heisenberg Hamiltonian, namely

$$\chi^{-+}_{ll'} = \langle\langle S^{-}_{l}(t) \, ; \, S^{+}_{l'}(0) \rangle\rangle \qquad (2.2.6)$$

and using Eqs (2.1.4) and (2.2.5), we make the observation that $\chi^{-+}_{ll'}$ is directly related to the Green's function of the Heisenberg Hamiltonian, given by

$$G^{b}_{ll'} = \langle\langle c_{l} \, ; \, c^{*}_{l'} \rangle\rangle \qquad (2.2.7)$$

ie

$$G^{b}_{ll'} = \langle\langle S^{-}_{l}(t) \, ; \, S^{+}_{l'}(0) \rangle\rangle \qquad (2.2.8)$$

We now set out to solve for $G_{ll'}$. Let $\{\psi_l^{(s)}\}$ represent the complete set of real eigenvectors of the matrix D^o and $\{\omega_s\}$ $(\hbar = 1)$ its corresponding set of eigenvalues ie

$$\sum_{l'} D^o_{ll'} \psi_{l'}^{(s)} = \omega_s \psi_l^{(s)} \tag{2.2.9}$$

with $\{\psi_l^{(s)}\}$ satisfying the orthonormality and closure condition,

$$\sum_l \psi_l^{(s)} \psi_{l'}^{(s')} = \delta_{ss'}$$

$$\sum_s \psi_l^{(s)} \psi_{l'}^{(s)} = \delta_{ll'} \tag{2.2.10}$$

$\{\psi_l^{(s)}\}$ can now be taken as the basis for a new set of eigenvectors which correspond to new operators $\overset{*}{a}_s$ and a_s, such that

$$\overset{*}{c}_l = \sum_s \psi_l^{(s)} \overset{*}{a}_s$$

$$c_l = \sum_s \psi_l^{(s)} a_s \tag{2.2.11}$$

$(\overset{*}{\psi} = \psi)$

Substituting Eqs (2.2.11) into Eq (2.2.5), we have

$$H^{o} = \sum_{l,l'} D^{o}_{ll'} \sum_{s} \psi_{l}^{(s)*} c_{s}^{*} \sum_{s'} \psi_{l'}^{(s')} c_{s'}$$

$$= \sum_{s} \omega_{s} c_{s}^{*} c_{s} \qquad (2.2.12)$$

Thus, we have formally diagonalized the Heisenberg Hamiltonian H^{o}.

The bulk spin-wave Green's function $G^{b}_{ll'}(\omega)$ for the infinite Heisenberg ferromagnet can now be defined as

$$G^{b}_{ll'}(\omega) = [\omega\, \delta_{ll'} - D^{o}_{ll'}]^{-1} \qquad (2.2.13)$$

which when expanded in terms of the eigenfunctions of D^{o}, takes the form

$$G^{b}_{ll'}(\omega) = \sum_{s} \frac{\psi_{l}^{(s)}\ \psi_{l'}^{(s)}}{\omega - \omega_{s}} \qquad (2.2.14)$$

provided that zero is not an eigenvalue of it.

If the wave-vector $\underline{k}$ is determined by the cyclic boundary condition and is uniformly distributed throughout the first Brillouin Zone of the crystal, then the eigenvectors are imaginary exponentials and Eq (2.2.14) may be written in the form

$$G^{b}_{11'}(\omega) = \frac{1}{N} \sum_{\underline{k}} \frac{e^{i\underline{k}.(\underline{x}_1-\underline{z}_{1'})}}{\omega - \omega_{\underline{k}}} \qquad (2.2.15)$$

where $\omega_{\underline{k}}$ is the 'bulk spin-wave excitation energy' given by

$$\omega_{\underline{k}} = \sum_{\substack{1 \\ (1 \neq 0)}} J_1 (1 - \cos \underline{k} \cdot \underline{x}_1) \qquad (2.2.16)$$

2.3 Bulk Spin-Wave Green's Function of An Itinerant Ferromagnet.

It was shown by Herring and Kittle (1951) that long wavelength spin-waves exist in any ferromagnet, in particular in an Itinerant one. In order to derive spin-wave energies in metallic ferromagnets, one usually calculates the response to a weak magnetic field that varies in space and time, namely the 'Transverse Dynamical Susceptibility.' (See T Izuyama, D J Kim and R Kubo ; 1963). Using the conventional definition of a Retarded Green's function (See Eq (1.3.3), the dynamical spin susceptibility can be defined in terms of spin-densities as follows:

$$\chi_{\alpha\beta}(\underline{k},\omega) = \lim_{\varepsilon\to 0+} \int_{-\infty}^{\infty} \langle\langle S_\alpha(\underline{k},t) \,;\, S_\beta(-\underline{k}) \rangle\rangle \; e^{-i\omega t-\varepsilon t} \, dt \tag{2.3.1}$$

S_α, S_β are the spin-densities of electrons with spin α and β respectively ; given by

$$S(\underline{k}) = \sum_{\underline{k}'} F(\underline{k},\underline{k}') \left(a^*_{\underline{k}+\underline{k}'} \, \hat{\sigma} \, a_{\underline{k}'}\right) \tag{2.3.2}$$

$$S(\underline{k},t) = \sum_{\underline{k}} F(\underline{k},\underline{k}') \left(a^*_{\underline{k}+\underline{k}'}(t) \, \hat{\sigma} \, a_{\underline{k}'}(t)\right)$$

Where $a_{\underline{k}}$, $a^*_{\underline{k}}$ are the two-component annihilation and creation operators of a Bloch-state $\underline{k}$; $\hat{\sigma}$ is the Pauli-matrix, and $F(\underline{k},\underline{k}')$ is the form-factor defined by

$$F(\underline{k},\underline{k}') = \sum_{\underline{k}'} e^{-i\underline{k}' \cdot \underline{R}} \int_{-\infty}^{\infty} w^{*}(\underline{r})\, w(\underline{r} + \underline{R})\, e^{-i\underline{k} \cdot \underline{r}}\, d\underline{r} \qquad (2.3.3)$$

which may be put as an approximation $F(\underline{k})$ if the overlap integrals of Wannier functions w for $\underline{R} \neq \underline{0}$ ($\underline{R}$ is the vector denoting the lattice site.) are ignored, ie

$$F(\underline{k},\underline{k}') \simeq F(\underline{k}) = \int_{-\infty}^{\infty} w^{*}(\underline{r})\, w(\underline{r})\, e^{-i\underline{k} \cdot \underline{r}}\, d\underline{r} \qquad (2.3.4)$$

This is substantially the form-factor of the 3d-atomic orbital using a tight-binding approximation. Eq (2.3.1) can now be reduced

$$\chi_{\alpha\beta}(\underline{k},\omega) = |\, F(\underline{k})\, |^{2}\ \chi'_{\alpha\beta}(\underline{k},\omega) \qquad (2.3.5)$$

with

$$\chi'_{\alpha\beta} = \int_{-\infty}^{\infty} \langle\langle S'_{\alpha}(\underline{k},t)\ ;\ S'_{\beta}(-\underline{k}) \rangle\rangle\ e^{-i\omega t}\, dt \qquad (2.3.6)$$

where S'_{α} , S'_{β} are defined by

$$S'(\underline{k}) = \sum_{\underline{k}'} a^{*}_{\underline{k}+\underline{k}'}\ \hat{\sigma}\ a_{\underline{k}'}$$

$$(2.3.7)$$

$$S'(\underline{k},t) = \sum_{\underline{k}'} a^{*}_{\underline{k}+\underline{k}'}(t)\ \hat{\sigma}\ a_{\underline{k}'}(t)$$

If we define

$$a_{\underline{k}+\underline{\kappa}} \equiv a_{\underline{k}} \qquad (2.3.8)$$

for any reciprocal lattice vector $\underline{\kappa}$, then $\chi'_{\alpha\beta}(\underline{k},\omega)$ is periodic in $\underline{k}$, with the periodicity of the reciprocal lattice vectors. Therefore, Eq (2.3.5) may be written as

$$\chi_{\alpha\beta}(\underline{k},\omega) = |F(\underline{k})|^2 \; \chi'_{\alpha\beta}(\underline{q},\omega) \qquad (2.3.9)$$

where

$$\underline{q} = \underline{k} - \underline{\kappa} \qquad (2.3.10)$$

is a Reduced wave-vector which lies in the first Brillouin Zone. The susceptibility $\chi'_{\alpha\beta}(q,\omega)$ which is the reduced form of $\chi_{\alpha\beta}(\underline{k},\omega)$, is appropriately known as the 'Reduced Susceptibility'. Here, we shall determine the component $\chi'_{-+}(\underline{q},\omega)$ of the Reduced susceptibility $\chi'_{\alpha\beta}(q,\omega)$, which is defined by

$$\chi'_{-+}(\underline{q},\omega) = \int_{-\infty}^{\infty} \langle\langle S'_{-}(\underline{q},t) \, ; \, S'_{+}(-\underline{q}) \rangle\rangle \, e^{-i\omega t} \, dt \qquad (2.3.11)$$

$$= i \int_{-\infty}^{\infty} \langle [S'_{-}(\underline{q},t) \, , \, S'_{+}(-\underline{q})] \rangle \, e^{-i\omega t} \, dt \qquad (2.3.12)$$

where the reduced spin-densities S'_- , S'_+ are defined by

$$S'_-(\underline{q},t) = \sum_{\underline{k}} a^*_{\underline{k}+\underline{q}\downarrow}(t) \; a_{\underline{k}\uparrow}(t)$$

$$S'_+(-\underline{q}) = \sum_{\underline{k}} a^*_{\underline{k}\uparrow}(0) \; a_{\underline{k}+\underline{q}\downarrow}(0) \tag{2.3.13}$$

With $\underline{q}$ given by Eq (2.3.10).

The Retarded Green's function $\langle\langle S'_-(\underline{q},t) \, ; \, S'_+(-\underline{q}) \rangle\rangle$ may now be determined by its equation of motion (See Eq (1.3.13)

$$i \frac{d}{dt} \langle\langle S'_-(\underline{q},t) \, ; \, S'_+(-\underline{q}) \rangle\rangle =$$

$$-\delta(t) \langle [S'_-(\underline{q},t) \, , \, S'_+(-\underline{q})] \rangle + \langle\langle [S'_-(\underline{q},t), H] \, ; \, S'_+(-\underline{q}) \rangle\rangle \tag{2.3.14}$$

where H is the Hamiltonian of the electron system.

For simplicity, we shall only consider the one-band Hubbard Hamiltonian H given by Eq (1.2.1). In the Bloch-representation, H can be written in the form

$$H = H_1 + H_2 \tag{2.3.15}$$

where

$$H_1 = \sum_{\underline{k}} \sum_{\sigma} E_{\underline{k}} \, n_{\underline{k}\sigma} \tag{2.3.16}$$

$$H_2 = U \sum_{\underline{k}_1,\underline{k}_2,\underline{k}_1',\underline{k}_2'} \; \sum_{\sigma} a^{*}_{\underline{k}_1,\sigma} \; a^{*}_{\underline{k}_2,-\sigma} \; a_{\underline{k}_2',-\sigma} \; a_{\underline{k}_1',\sigma} \tag{2.3.17}$$

where $E_{\underline{k}}$ is the energy of a Bloch-state and $n_{\underline{k}\sigma}$ is the occupation number of the state $\underline{k}\sigma$, σ being the spin-state, ie

$$n_{\underline{k}\sigma} = a^{*}_{\underline{k}\sigma} \; a_{\underline{k}\sigma} \; . \tag{2.3.18}$$

For our convenience we let

$$\theta_{\underline{k}}(\underline{q},t) = a^{*}_{\underline{k}+\underline{q}\downarrow}(t) \;\; a_{\underline{k}\uparrow}(t) \; . \tag{2.3.19}$$

Then, using Eqs (2.3.13) ; for each member of the R.H.S of Eq (2.3.14), we have

$$i \frac{d}{dt} \langle\langle \; \theta_{\underline{k}}(\underline{q},t) \; ; \; S'_{+}(-\underline{q}) \; \rangle\rangle =$$

$$= -\delta(t) \; \langle \; [\theta_{\underline{k}}(\underline{q},t) \; , \; S'_{+}(-\underline{q})] \; \rangle + \langle\langle \; [\theta_{\underline{k}}(\underline{q},t) \; , \; H] ; S'_{+}(-\underline{q}) \; \rangle\rangle \tag{2.3.20}$$

where

$$[\theta_{\underline{k}}(\underline{q})\ ,\ S'_{+}(-\underline{q})] \ = \ n_{\underline{k}+\underline{q}\downarrow}-n_{\underline{k}\uparrow} \qquad (2.3.21)$$

$$[\theta_{\underline{k}}(\underline{q})\ ,\ H_1] \ = \ (E_{\underline{k}} - E_{\underline{k}+\underline{q}})\theta_{\underline{k}}(\underline{q}) \qquad (2.3.22)$$

$$\begin{aligned}[\theta_{\underline{k}}(\underline{q})\ ,\ H_2] \simeq U \sum_{\underline{k}} \ & \theta_{\underline{k}+\underline{k}'}(\underline{q})\ \{-n_{\underline{k}+\underline{q}\downarrow}+n_{\underline{k}\uparrow}\} \\ & + \ \theta_{\underline{k}}(\underline{q})\ \{-n_{\underline{k}+\underline{k}'\uparrow} + n_{\underline{k}+\underline{q}+\underline{k}'\downarrow}\}\end{aligned} \qquad (2.3.23)$$

Further, the chain of successive Green's functions is cut off by the approximation

$$\langle\langle\, n_{\underline{k}\sigma}\ \theta_1(\underline{q},t)\ ;\ S'_{+}(-\underline{q})\,\rangle\rangle \ \simeq \ n_{\underline{k}\sigma}\ \langle\langle\, \theta_1(\underline{q},t)\ ;\ S'_{+}(-\underline{q})\,\rangle\rangle \qquad (2.3.24)$$

This is known as the Random Phase Approximation (RPA).

Now, using Eqs (2.3.21), (2.3.22), (2.3.23) and (2.3.24) ; The equation of motion (2.3.20) becomes

$$i \frac{d}{dt} \langle\langle \theta_{\underline{k}}(\underline{q},t) \; ; \; S'_{+}(-\underline{q}) \rangle\rangle =$$

$$-\delta(t) \{n_{\underline{k}+\underline{q}\downarrow} - n_{\underline{k}\uparrow}\} \quad +$$

$$(\epsilon_{\underline{k}\uparrow} - \epsilon_{\underline{k}+\underline{q}\downarrow}) \langle\langle \theta_{\underline{k}}(\underline{q},t) \; ; \; S'_{+}(-\underline{q}) \rangle\rangle \quad +$$

$$U(n_{\underline{k}\uparrow} - n_{\underline{k}+\underline{q}\downarrow}) \sum_{\underline{k}'} \langle\langle \theta_{\underline{k}+\underline{k}'}(\underline{q},\underset{+}{t}) \; ; \; S'_{+}(-\underline{q}) \rangle\rangle \tag{2.3.25}$$

where

$$\epsilon_{\underline{k}\sigma} = E_{\underline{k}} - U \sum_{\underline{k}'} n_{\underline{k}+\underline{k}'} \; , \; \sigma \tag{2.3.26}$$

is the HF one-particle energy with spin σ.

Finally, using the Fourier transformation of $\langle\langle \theta_{\underline{k}}(\underline{q},t) \; ; \; S'_{+}(-\underline{q}) \rangle\rangle$ and summing over all wave numbers, we obtain the solution

$$\chi'_{-+}(\underline{q},\omega) = \frac{\Gamma_{-+}(\underline{q},\omega)}{I - U\,\Gamma_{-+}(\underline{q},\omega)} \tag{2.3.27}$$

where $\Gamma_{-+}(\underline{q},\omega)$ is defined by

$$\Gamma_{-+}(\underline{q},\omega) = \frac{1}{N} \sum_{\underline{k}} \frac{n_{\underline{k}\uparrow} - n_{\underline{k}+\underline{q}\downarrow}}{\epsilon_{\underline{k}+\underline{q}\downarrow} - \epsilon_{\underline{k}\uparrow} - \omega} \tag{2.3.28}$$

The poles of Eq (2.3.27) lead to excitation energies of the system. This implies that there are two types of singularities in $\chi'_{-+}(\underline{q},\omega)$:

a) Singularities of $\Gamma_{-+}(\underline{q},\omega)$ itself, which lead to the 'stoner excitation energies'. These energies form a 'branch-cut' along the real part of the frequency ω , and depend on $\underline{q}$.

b) Singularities which arise when

$$U\,\Gamma_{-+}(\underline{q},\omega) = 1 \qquad (2.3.29)$$

ie

$$U \sum_{\underline{k}}^{*} \frac{1}{\epsilon_{\underline{k}+\underline{q}\downarrow} - \epsilon_{\underline{k}\uparrow} - \omega} = 1 \qquad (2.3.30)$$

(See Appendix A).

These are isolated poles along the real part of ω that also depend on $\underline{q}$ and are called the 'bulk spin-wave excitation energies'.

2.4 An Effective Heisenberg Ferromagnet for Spin-Waves.

In this section, we shall aim at deriving an effective Heisenberg Hamiltonian H^{eff} for spin-waves in an Itinerant ferromagnet. This approach has the advantage that the formulation in terms of effective exchange integrals, namely J^{eff}, is physically very simple, and the effect of impurities or of a surface on spin-waves can be easily included.

We begin by noting that H^{eff} is completely determined by its resolvent G, ie

$$G = (\omega I - H^{eff})^{-1} \tag{2.4.1}$$

and the resolvent G is in turn completely determined by the energy spectrum of magnetic excitations of the system.

We saw in section 2.2 that the resolvent G for a Heisenberg ferromagnet is in fact equivalent to its transverse susceptibility. Similarly, for an Itinerant ferromagnet, the transverse dynamical susceptibility determines an effective Hamiltonian by

$$\chi_{-+} = (\omega I - H^{eff})^{-1} \tag{2.4.2}$$

where χ_{-+} is given in RPA by Eq (2.3.27)

(We have dropped the (') sign in χ'_{-+}).

For low excitation energies ω and small $\underline{q}$, $\Gamma_{-+}(\underline{q},\omega)$ of Eq (2.3.28) can be expanded in powers of ω. Using the Taylor's expansion, we have

$$\Gamma_{-+}(\underline{q},\omega) \simeq \Gamma_{-+}(\underline{q},0) + \frac{\omega}{\Delta} + O(\frac{1}{\Delta^2}) \qquad (2.4.3)$$

where Δ is the exchange splitting.

Substituting Eq (2.4.3) into Eq (2.3.29) and writing it in the Wannier representation using

$$\Gamma_{-+}(\underline{q},o) = \frac{1}{N} \sum_{1,1'} \Gamma^{-+}_{11'} (\omega=0)\, e^{i\underline{q}.(\underline{x}_1-\underline{x}_{1'})} \qquad (2.4.4)$$

we have

$$1 - U\Gamma_{-+}(\underline{q},\omega) \simeq \frac{1}{N}\frac{1}{\Delta} \sum_{1,1'} \{\omega\delta_{11'} + \Delta\,\delta_{1,1'} - U\Delta\Gamma^{-+}_{11'}(\omega=0)\}e^{i\underline{q}.(\underline{x}_1-\underline{x}_{1'})} \qquad (2.4.5)$$

where $\Gamma^{-+}_{11'}(\omega=0)$ is the static unenhanced susceptibility of the Itinerant ferromagnet in the Wannier representation.

Since the Goldstone mode $\omega=0$ is always a pole of Eq (2.3.27), we have

$$1 - U\Gamma_{-+}(\underline{0},0) = 0 \tag{2.4.6}$$

Thus, using Eq (2.4.6) in Eq (2.4.5), we obtain

$$1 - U\Gamma_{ll}(0) = \sum_{\substack{l' \\ (l' \neq l)}} U\Gamma_{ll'}(0) \tag{2.4.7}$$

which shows that the approximate resolvent of one Itinerant ferromagnet in the Wannier representation takes the form

$$G^{itin} = (\omega\, \delta_{ll'} - B_{ll'})^{-1} \tag{2.4.8}$$

where

$$B_{ll'} = U\Delta\Gamma_{ll'}(0) \tag{2.4.9}$$

$$B_{ll} = -\sum_{\substack{l' \\ (l' \neq l)}} B_{ll'} \tag{2.4.10}$$

Comparing Eqs (2.2.3) and (2.2.4) with Eqs (2.4.9) and (2.4.10), it is quite clear that G^{itin} is equivalent to the resolvent of an effective Heisenberg Hamiltonian with exchange integrals

$$J^{eff}_{ll'} = U\Delta\Gamma_{ll'}(\omega=0) . \qquad (2.4.11)$$

As mentioned at the beginning of Sec 2.4, our aim was to derive an effective Heisenberg Hamiltonian for an Itinerant ferromagnet, so that it could be used to calculate the spin-wave energies in such a ferromagnet. This is achieved by finding an approximate Green's function for the Hamiltonian of an Itinerant ferromagnet using RPA method. By doing this, we arrive at an expression in terms of the static unenhanced susceptibility of the Itinerant ferromagnet which leads to a Green's function with the same structure as the Green's function of a Heisenberg ferromagnet. It is then justified to replace the Hubbard Hamiltonian of an Itinerant ferromagnet by an equivalent Heisenberg Hamiltonian where the exchange integrals J are now determined from the band-structure. We choose to call these parameters, effective exchange integrals and denote them by J^{eff}. However, it should be noted that, this procedure gives good results only when the magnetic excitations are of low energy and long wavelength, ie small ω and q.

Moreover, we are now in a position to take advantage of the results obtained by Wolfram and Callaway (See T Wolfram & J Callaway ; 1963) which deals with an impurity in a ferromagnetic insulator, ie we can treat an isolated impurity in an Itinerant ferromanget as a perturbation to the bulk problem (See J Mathon ; 1984). Similarly, we can use the results of De Wames and Wolfram: (See R E De Wames & T Wolfram ; 1969) to map the surface problem for an Itinerant ferromagnet onto an equivalent surface problem for a Heisenberg one.

It is also important to note that it is possible to show $J^{eff}_{ll'}$ (which depend only on $|\underline{x}_l - \underline{x}_{l'}| = \underline{R}$) are large only for distances $|\underline{R}|$ of the order of hopping of electrons from one atom to the next. It was shown by Mathon (1983) that for a strong ferromagnet with a free-electron (parabolic) band, $J^{eff}(\underline{R})$ decays exponentially with distance. Exponential decay of $J^{eff}(\underline{R})$ for strong ferromagnets makes the use of an effective Heisenberg model attractive since problems involving inhomogeneties such as impurities and surfaces are more easily handled within the Heisenberg model with a relatively short-range exchange.

In the proceding section, we shall address this problem for a strong tight-binding Itinerant ferromagnet and demonstrate that it is quite sufficient to consider only the nearest neighbour J^{eff} in the limit $\Delta >> E_F$.

2.5 Short-Range of Effective J for a strong Tight-binding Itinerant Ferromagnet.

Our model is a strong Itinerant ferromagnet in the tight-binding approximation, with the condition $E_F/\Delta << 1$ where E_F and Δ are the Fermi-level and the exchange-splitting respectively.

We first consider the HF one-electron Green function (See Sec 1.3.5) for a bulk ferromagnetic crystal, given by

$$G^{\sigma}_{\text{bulk}}(\underline{R} = \underline{R}_l - \underline{R}_{l'}) = \frac{1}{N} \sum_{\underline{q}} G^{\sigma}_{\text{bulk}}(\underline{q})\, e^{i\underline{q}.\underline{R}} \qquad (2.5.1)$$

where for a strong-ferromagnet, the down-spin propagators $G^{\downarrow}_{\text{bulk}}(\underline{R})$ are real. (Since there are no particles in the down-spin band ie $\text{Im}\, G^{\downarrow}_{\text{bulk}} = 0$). Using Eq (2.5.1) we have

$$G^{\downarrow}_{\text{bulk}}(\underline{R}) = \frac{1}{N} \sum_{\underline{q}} G^{\downarrow}_{\text{bulk}}(\underline{q})\, e^{i\underline{q}.\underline{R}} \qquad (2.5.2)$$

where from Eqs (1.2.61) and (1.2.62), we now define,

$$G^{\downarrow}_{\text{bulk}}(\underline{q}) = \frac{1}{\omega - \Delta - \omega_{\underline{q}}} \qquad (2.5.3)$$

with

$$\omega_{\underline{q}} = - T \sum_{\underline{R}} e^{i\underline{q}.\underline{R}_{n.n}} \qquad (2.5.4)$$

$\underline{R}_{n.n}$ is the position-vector between two nearest neighbour atomic sites and T is the electron hopping integral.

Using Eq (2.5.3) in Eq (2.5.2), we have

$$G^{\downarrow}_{\text{bulk}}(\underline{R}) = \frac{1}{N} \sum_{\underline{q}} (\omega - \Delta - \omega_{\underline{q}})^{-1} e^{i\underline{q}.\underline{R}} \tag{2.5.5}$$

For $E_F/\Delta << 1$, we may expand $(\omega - \Delta - \omega_{\underline{q}})^{-1}$ in powers of ω/Δ. Hence,

$$(\omega - \Delta - \omega_{\underline{q}})^{-1} = -\frac{1}{\Delta}(1 + \frac{\omega}{\Delta}) - \frac{1}{\Delta^2}\omega_{\underline{q}} + O[(\frac{\omega}{\Delta})^3] \tag{2.5.6}$$

Substituting Eq (2.5.6) into Eq (2.5.5) and using Eq (2.5.4), we have

$$G^{\downarrow}_{\text{bulk}}(\underline{R}) = -\frac{1}{\Delta}(1 + \frac{\omega}{\Delta}) \frac{1}{N} \sum_{\underline{q}} e^{i\underline{q}.\underline{R}} - \frac{T}{\Delta^2} \sum_{\underline{R}} \frac{1}{N} \sum_{\underline{q}} e^{i\underline{q}.(\underline{R}-\underline{R}_{n.n})}$$

$$+ O[(\frac{\omega}{\Delta})^3] \tag{2.5.7}$$

which gives

$$G^{\downarrow}_{\text{bulk}}(\underline{R}) = -\frac{1}{\Delta}(1 + \frac{\omega}{\Delta}) \delta_{\underline{R},\underline{O}} - \frac{T}{\Delta^2} \sum_{\underline{R}} \delta_{\underline{R},\underline{R}_{n.n}} + O[(\frac{\omega}{\Delta})^3] \tag{2.5.8}$$

where

$$\delta_{\underline{R}_l,\underline{R}_{l'}} = \frac{1}{N} \sum_{\underline{q}} e^{i\underline{q}.(\underline{R}_l - \underline{R}_{l'})} \tag{2.5.9}$$

is the Kronecker delta.

From the definition of the Heisenberg Hamiltonian of Sec 2.2, it is clear that $J^{eff}_{ll'}$ are the off-diagonal elements of their appropriate Green's function. Thus, looking at Eq (2.5.8), the term with $\delta_{\underline{R},\underline{R}_{n.n}}$ becomes the leading term and $G^{\downarrow}_{bulk}$ takes the form

$$G^{\downarrow}_{bulk}(\underline{R}_{n.n}) = -\frac{T}{\Delta^2} \tag{2.5.10}$$

From Eq (2.4.11), we have

$$J^{eff}_{bulk}(\underline{R}) = U\Delta\Gamma_{bulk}(\underline{R}) \tag{2.5.11}$$

where for a strong ferromagnet, Γ_{bulk} is given by

$$\Gamma_{bulk} = -\frac{1}{\pi} \int_{-\infty}^{E_F} \mathrm{Re}\, G^{\downarrow}_{bulk}(\omega)\, \mathrm{Im}\, G^{\uparrow}_{bulk}(\omega)\, d\omega. \tag{2.5.12}$$

Thus, using Eqs (2.5.10), (2.5.11) and (2.5.12) we have

$$J^{eff}_{bulk}(\underline{R}_{n.n}) = -\frac{1}{\pi}\int_{-\infty}^{E_F} \Delta^2 \left(\frac{-T}{\Delta^2}\right) \text{Im } G^{\uparrow}_{bulk}(\underline{R}_{n.n},\omega)\, d\omega$$

$$= \frac{T}{\pi}\int_{-\infty}^{E_F} \text{Im } G^{\uparrow}_{bulk}(\underline{R}_{n.n},\omega)\, d\omega \qquad (2.5.13)$$

where

$$\text{Im } G^{\uparrow}_{bulk}(\underline{R}_{n.n}) = -\frac{E}{TZ}\,\text{Im}(G^{\uparrow}_{bulk}(\underline{R} = \underline{0})) \qquad (2.5.14)$$

(See Appendix B) , and

$$U\Delta \simeq \Delta^2 \quad , \quad E_F << \Delta$$

We have therefore shown that the effective exchange integrals within the range of electron hopping tend to a finite limit for $\Delta/E_F >> 1$ and all the other exchange integrals tend to zero. From Eq (2.5.10), we see that the range of J^{eff}_{bulk} for a tight-binding band with nearest neighbour electron hopping is determined by the range of the electron hopping T. Hence, it is possible to extend this result to a more general tight-binding band with longer electron hopping. Although this formal proof holds only for strong ferromagnets, the tight-binding calculations of Finnis and Pettifor (1984) of the response functions for paramagnets show that they are appreciable only over distances of the order of electron hopping.

Chapter 3 Effect of Surface on Spin-Waves.

3.1 Introduction 3.

There is renewed interest in the study of 'surface spin-waves', primarily, since the surface magnetization and its temperature dependence are now directly measurable, (see J C Walker et al; 1984 - D T Pierce et al; 1982 - S Alvarado et al; 1982). At low-temperatures, the surface magnetization is determined by spin-waves.

In this chapter, we examine the effect of a surface on both metallic (itinerant) and non-metallic (Heisenberg) ferromagnets. We shall then study spin-waves and their magnetic properties in such systems and, finally, as we did for bulk spin-waves, we shall map the surface spin-wave problem for a metal onto an effective Heisenberg model. We shall also include the study of impurities on a ferromagnetic surface with a view to investigate the behaviour of spin-waves in such structures.

3.2 Surface Spin-Wave Green's Function of a Heisenberg Magnetic Insulator.

There are many theoretical studies of the effect of surface on spin-waves in magnetic insulators. Here, we shall consider the Heisenberg model of a magnetic insulator described in Sec 2.1, where the spins on sites l and l' are coupled by an exchange interaction $- J_{ll'} \underline{S}_l \cdot \underline{S}_{l'}$.

Our approach here is that of De Wames and Wolfram's (See R E De Wames and T Wolfram; 1969). We introduce the surface plane by cutting the exchange integrals $J_{ll'}$ across a cleavage plane, ie we set equal to zero all the $J_{ll'}$ between spins on atoms which are on adjacent sides of the plane $z = \frac{1}{2} a$, so that all the $J_{ll'}$'s between atoms in the planes $z = 0$ and $z = a$ are zero. This procedure is referred to as the 'geometric effect' of the surface.

We begin with a Hamiltonian for a semi-infinite ferromagnetic crystal with a surface described above,

$$H = H^o + V \qquad (3.2.1)$$

where H^o is given by Eq (2.2.5) and V represents the geometric effect of surface,

$$V = \sum_{l,l'} V_{ll'} \, C_l^{*} \, C_{l'} \tag{3.2.2}$$

with

$$V_{ll'} = (\delta_{l_{3,0}} \, \delta_{l'_{3,1}} + \delta_{l_{3,1}} \, \delta_{l'_{3,0}}) \, J_{ll'} \qquad l \neq l' \tag{3.2.3}$$

$$V_{ll} = - \sum_{l'} V_{ll'} \tag{3.2.4}$$

$$(l' \neq l)$$

where C_l^{*} and $C_{l'}$ are given by Eqs (2.1.5).

The surface spin-wave Green's function $G^{S_1}_{ll'}(\omega)$ for the semi-infinite Heisenberg ferromagnet can now be defined as

$$G^{S_1}_{ll'}(\omega) = [\omega\delta_{ll'} - D_{ll'}]^{-1} \tag{3.2.5}$$

where

$$D_{ll'} = D^{o}_{ll'} + V_{ll'} \tag{3.2.6}$$

To obtain the Green's function $G^{S1}_{11'}(\omega)$, we note, using Eq (2.2.13) that it can be written as an inverse matrix

$$G^{S1} = [\omega I - D^{o} - V]^{-1}$$

$$= [(G^{b})^{-1} - V]^{-1}$$

$$\text{ie} \quad G^{S1} = [I - G^{b}V]^{-1} G^{b} \tag{3.2.7}$$

where the elements of the matrix G^{b} are given by Eq (2.2.15).

With the intention of mapping the surface spin-waves problem of an itinerant ferromagnet onto an effective Heisenberg model, we now study the effect of our surface to G^{S1} when we renormalize it. This renormalization is done by allowing the exchange constant coupling spins parallel ($J_{||}$) and perpendicular ($J_{\perp}$) to the crystal surface, to deviate from their bulk values (J^{b}), in the first two atomic planes adjacent to the surface. (It should be noted that the deviation of $J_{||}$ and $J_{\perp}$ from J^{b}, only in the first two atomic planes, is sufficient for a strong ferromagnet which will be studied in Sec 3.3).

By letting $V_{11} = 0$, ie ignoring the diagonal elements of the geometric effect, we can use Kalkstein & Soven's result and write

$$G^{S1}_{ij}(\underline{k}_{||}) = G^{b}(|i-j|, \underline{k}_{||}) - G^{b}(i+j, \underline{k}_{||}) \tag{3.2.8}$$

in the mixed Bloch-Wannier representation.

The only purpose of ignoring V_{11} is that we can express G^{S1} simply in terms of the bulk Green's function G^b. However, these elements shall be included later in the renormalized Green's function where the effect of $J_{||}$, $J_{\perp} \neq J^b$ is considered. This effect will lead to a perturbation to G^{S1}, which is presented in the form of a (2x2) matrix called w^{Heis}. Hence, using a Dyson equation, the renormalized Green's function G^{S2} can be written in the form

$$G^{S2} = G^{S1} + G^{S1} w^{Heis} G^{S2} \qquad (3.2.9)$$

or more conveniently

$$G^{S2} = \frac{G^{S1}}{I - G^{S1} w^{Heis}} \qquad (3.2.10)$$

where G^{S1} is calculated by Eq (3.2.8). It is easy to show that the elements of w^{Heis} are given by

$$w_{11} = -4 \Lambda q (1 - \epsilon_{||}) - (1 - \epsilon_{\perp}) \qquad (3.2.11)$$

$$w_{12} = 1 - \epsilon_{\perp} \qquad (3.2.12)$$

$$w_{22} = -w_{12} \; . \qquad (3.2.13)$$

(See R E De Wames and T Wolfram ; 1969), where

$$\epsilon_{||} = \frac{J_{||}}{J^b} \qquad (3.2.14)$$

$$\epsilon_{\perp} = \frac{J_{\perp}}{J^b} \qquad (3.2.15)$$

$$\Lambda_q = 1 - \tfrac{1}{2}(\cos q_x a + \cos q_y a) \qquad (3.2.16)$$

As promised earlier, we now include the diagonal elements of V in w^{Heis} which is equivalent to adding a (2x2) matrix $\begin{bmatrix} -1 & 0 \\ 0 & 0 \end{bmatrix}$ to w^{Heis}.

We note that this will only affect the matrix element w_{11} which now becomes

$$w_{11} = -4\,\Lambda q\,(1-\epsilon_{||}) - 1 - (1-\epsilon_{\perp}) \qquad (3.2.17)$$

3.3 Effect of Surface on the Spin-Wave Green's Function of an Itinerant Ferromagnet.

The measurements made on metallic ferromagnets require interpretation in terms of the Itinerant model of ferromagnetism. However, there are no such calculations of the effect of surface on bulk spin-waves and, information on surface spin-waves is very limited.

Surface spin-waves were studied previously by Griffin and Gumbs. They were forced (by the complexity of the surface problem in metals) to adopt the classical infinite barrier model (CIBM) which assumes that the static electron-density in a metal remains constant right up to its surface. However, recent band-structure calculations (See H Krakever et al ; 1983) indicate that this assumption is not valid in transition metals such as Ni and we shall show that CIBM is not a realistic model of metals.

In this section, we describe a real space approach to the problem of spin-waves in a simple cubic tight-binding Itinerant ferromagnet with a (100) surface, using the simplest one-band Hubbard model of an Itinerant ferromagnet with surface, in the random phase approximation. As in Sec 3.2, our semi-infinite crystal contains both the geometric and the renormalization effects when the surface is introduced. The geometric effect itself leads to Friedel oscillations in the electron-density. To preserve layer-by-layer charge neutrality, we have to compensate this effect by an adjustable potential V.

The Hamiltonian of our semi-infinite crystal then becomes

$$H' = H + V \qquad (3.3.1)$$

where H is given by Eq (1.2.1) where the summation indices are now over the semi-infinite crystal only. The perturbation V is given by

$$V = \sum_{i,\sigma} V_i \, n_{i\sigma} \qquad (3.3.2)$$

with

$$V_i = \begin{cases} 0 & \text{in the bulk.} \\ V_o & \text{in the surface.} \end{cases} \qquad (3.3.3)$$

Eq (3.3.1) in the Wannier representation becomes

$$H' = \sum_{i,j} \sum_{\sigma} E_{ij} \, c^{*}_{i\sigma} \, c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + V_o \sum_{i,\sigma} n_{i\sigma} \qquad (3.3.4)$$

where E_{ij} is the hopping integral given by

$$E_{ij} = \frac{1}{N} \sum_{\underline{q}} E_{\underline{q}} \, e^{i\underline{q}.(\underline{R}_i - \underline{R}_j)} \qquad (3.3.5)$$

It was shown by Mathon and Al-Asadi (1981), that poles of the transverse susceptibility matrix $\chi^{s}_{ij}(\omega)$ determine the surface spin-wave energies, where χ^{s}_{ij} is given by

$$\chi^{s}_{ij}(\omega) = \chi^{o}_{ij}(\omega) + \sum_{n} \chi^{o}_{in}(\omega) \; U_{n} \; \chi^{s}_{nj}(\omega) \tag{3.3.6}$$

With χ^{o}_{ij} being the unenhanced surface susceptibility of non-interacting particles moving in a spin-dependent HF potential

$$V_{i\sigma} = V + I \; n_{i,-\sigma} \tag{3.3.7}$$

where V is the surface potential (or core-shift) given by Eq (3.3.3) and $I \; n_{i,-\sigma}$ is the HF exchange potential. The HF potential is highly inhomogeneous since both V and the cleavage plane perturb the electron-density near the surface. As a result, the kernel χ^{o}_{ij} is an off-diagonal matrix (See Mills et al; 1972 and Muscat et al; 1975). The solution of Eq (3.3.6) is thus equivalent to the inversion of a general (off-diagonal) infinite matrix. All the previous attempts at solving it without drastic approximations have failed (since χ^{o}_{ij} is off-diagonal both in the Wannier and Bloch representations).

From Sec 2.3, we have the standard unenhanced susceptibility of a bulk Itinerant ferromagnet $\Gamma(q,\omega)$ given by Eq (2.3.28) which is a diagonal matrix in the Bloch-representation. Using the translational symmetry in the direction parallel to the surface, we treat the surface as a perturbation to the bulk problem. (This is a method usually adopted for magnetic insulators, (See D L Mills and A A Maradudin; 1967).

Thus, we can write

$$\chi^{o}_{ij}(\underline{q}_{||},\omega) = \Gamma_{ij}(\underline{q}_{||},\omega) + \Lambda_{ij}(\underline{q}_{||},\omega) \qquad (3.3.8)$$

where Γ in the mixed Bloch-Wannier representation is given by

$$\Gamma_{ij}(\underline{q}_{||},\omega) = \frac{1}{N_{\perp}} \sum_{q_{\perp}} \Gamma(q_{\perp},\omega)\, e^{iq_{\perp}\cdot(\underline{R}_i-\underline{R}_j)} \qquad (3.3.9)$$

with $N_{\perp}$ denoting the number of atomic planes parallel to the surface and $q_{\perp}$, the wave-vector perpendicular to the surface. Λ_{ij} denotes the perturbation to the bulk.

Writing Eq (3.3.6) in the mixed Bloch-Wannier representation, we have

$$\chi^{s}_{ij}(\underline{q}_{||},\omega) = \chi^{o}_{ij}(\underline{q}_{||},\omega) + \sum_{n} \chi^{o}_{in}(\underline{q}_{||},\omega)\, U_n\, \chi^{s}_{nj}(\underline{q}_{||},\omega) \qquad (3.3.10)$$

where $\chi^{o}_{ij}(\underline{q}_{||},\omega)$ is now given by Eq (3.3.8).

We now set out to determine Λ_{ij}. It can be seen from Eq (3.3.8) that Λ is just the differrence between the non-interacting surface susceptibility χ^o and the bulk Γ, ie

$$\Lambda = \chi^o - \Gamma \tag{3.3.11}$$

In order to solve for Λ, we follow the same approach as in Sec 3.2, ie we shall first consider the geometric effect of the surface. For a strong ferromagnet, Γ is now determined by Eq (2.5.12) and the kernel χ^o by

$$\chi^o_{ij}(\omega) = -\frac{1}{\pi}\int_{-\infty}^{E_F} \mathrm{Re}\ G^{o\downarrow}_{ij}(E+\omega)\ \mathrm{Im}\ G^{o\uparrow}_{ij}(E)\ dE. \tag{3.3.12}$$

where $G^{o\sigma}_{ij}$ is the one-electron surface propagator given by

$$G^{o\sigma}_{ij}(\underline{q}_{||},E) = G^{\sigma}_{bulk}(|i-j|,\underline{q}_{||},E) - G^{\sigma}_{bulk}(i+j,\underline{q}_{||},E) \tag{3.3.13}$$

where

$$G^{\sigma}_{bulk}(n,\underline{q}_{||},E) = \frac{1}{N}\sum_{q_\perp} \frac{e^{iq_\perp na}}{E - E^{\sigma}(\underline{q}_{||},q_\perp)} \tag{3.3.14}$$

(See D Kalkstein and P Soven ; 1971).

i,j label atomic planes parallel to the surface; $q_{||}$ and $q_{\perp}$ are the components of the wave-vector parallel and perpendicular to the surface and $E^{\sigma}(q_{||},q_{\perp})$ is the bulk one-electron energies moving in the HF potential.

Griffin and Gumbs took the crudest approximation of Λ. They assumed that all the matrix elements of χ^{o}_{ij} for $i,j \geqslant 1$ are equal to the elements of the bulk Γ_{ij}. (this is known as the CIBM). It is clear that CIBM is not a realistic model for metals since the quantum interference effect of the surface is overlooked. (They determine the kernel χ^{o} using the propagators G^{bulk} rather than G^{o}).

A more realistic surface is the one where the effect of the core-shift V_o and of the HF corrections are included. This yields a better surface Green's function $\bar{G}^{o\sigma}$, whose matrix element $\bar{G}^{o\sigma}_{ij}$ is given by

$$\bar{G}^{o\sigma}_{ij} = G^{o\sigma}_{ij} + \frac{G^{o\sigma}_{io}\, V^{\sigma}_{o}\, G^{o\sigma}_{oj}}{1 - G^{o\sigma}_{oo}\, V^{\sigma}_{o}} . \tag{3.3.15}$$

where V^{σ}_{o} is the HF potential in the surface plane, and we have assumed that n^{σ}_{s} differs from n^{σ}_{b}, ie

$$V^{\sigma}_{o} = V_o + I^{eff}_{o}\,(n^{-\sigma}_{s} - n^{-\sigma}_{b}) \tag{3.3.16}$$

Eqs (2.5.12), (3.3.12) and (3.3.15) determine completely the perturbation matrix Λ.

Writing Eq (3.3.10) in an operator form, we have

$$\chi^s = \chi^o + \chi^o U_o \chi^s \tag{3.3.16}$$

Thus,

$$\chi^s = \frac{\chi^o}{I - \chi^o U_o} \tag{3.3.18}$$

where the poles of the secular equation

$$I - \chi^o U_o = 0 \tag{3.3.19}$$

give the surface spin-wave energies.

It is easy to show that the spin-wave Green's function of a semi-infinite ferromagnet $\bar{G}^s$ satisfies the following Dyson equation,

$$\bar{G}^s = G^b + G^b w^{itin} \bar{G}^s \tag{3.3.20}$$

where

$$G^b = [I - U_o \Gamma)^{-1} \tag{3.3.21}$$

$$\bar{G}^s = [I - U_o(\Gamma + \Lambda)]^{-1} \tag{3.3.22}$$

and the surface perturbation w^{itin} is given by

$$w^{itin} = U_o(\chi^o - \Gamma\ ) \qquad (3.3.23)$$

We now set out to find w^{itin} that would make the Dyson equation (3.3.20) solvable. With Eq (2.5.11) in mind, we note that Eq (3.3.23) can be written in the form

$$w^{itin} = \frac{1}{\Delta}(J^{eff} - J_b{}^{eff}) \qquad (3.3.24)$$

which suggests that the effect of Friedel oscillations and HF corrections can be regarded as a renormalization of the bulk effective exchange integrals near the surface. (J^{eff} is the surface exchange integral). We shall consider such renormalization only in the first two atomic planes, ie we consider a truncated (2x2) matrix w^{itin}. We note that Eq (3.3.20) is very similar to Eq (3.2.9) which is the Dyson equation for the Green's function of a conventional Heisenberg ferromagnet with exchange integrals in the surface $J_{||}$ and between the surface and adjacent plane $J_{\perp}$ different from J^b.

We shall now show that the matrix element w_{11}^{itin} has the same structure as the matrix element w_{11}^{Heis} given by Eq (3.2.11). In other words, it is possible to derive effective $\epsilon_{||}$ and $\epsilon_{\perp}$. This result can be proved exactly in the limit $\Delta \gg E_F$ and we shall now present the proof.

It follows from Eqs (2.5.12), (3.3.14) and (3.3.24) that w^{itin}_{11} is given by

$$w^{itin}_{11} = -U_o \frac{1}{\pi N} \sum_{\underline{k}} \int_{-\infty}^{E_F} \mathrm{Re}\ \bar{G}^{o\uparrow}_{oo}(E + \omega, \underline{k} + \underline{q}).\ \mathrm{Im}\bar{G}^{o\uparrow}_{oo}(E,\underline{k})$$

$$-\mathrm{Re}\ G^{b\uparrow}_{oo}(E + \omega, \underline{k} + \underline{q}).\mathrm{Im}\ G^{b\uparrow}_{oo}(E,\underline{k})]\ dE \quad (3.3.25)$$

It is now easy to show using the expansion (2.5.8) and keeping terms up to $(E_F/\Delta)^2$ that

$$\mathrm{Re}\ G^{b\uparrow}_{oo}\ (E + \omega, \underline{k} + \underline{q}) = -\frac{1}{\Delta} - \frac{1}{\Delta^2}\ (E + \omega + E_{\underline{q}}) \quad (3.3.26)$$

and

$$\mathrm{Re}\ \bar{G}^{o\uparrow}_{oo}(E + \omega, \underline{k} + \underline{q}) = -\frac{1}{\Delta}\ (\frac{n_b}{n_s}) - \frac{1}{\Delta^2}\ (\frac{n_b}{n_s})^2\ (E + \omega + E_{\underline{k}+\underline{q}})$$

$$+ \frac{1}{\Delta^2}\ E_o\ (\frac{n_b}{n_s})^2 \quad (3.3.27)$$

with

$$E_{\underline{q}} = -T \sum_{\underline{R}_{n.n}} e^{i\underline{q}.\underline{R}_{n.n}} \quad (3.3.28)$$

$\underline{R}_{n.n}$ is the position vector between two nearest neighbouring atoms.

Both Re $\bar{G}^{0\uparrow}_{00}$ and Re $G^{b\uparrow}_{00}$ have terms $\alpha\ \frac{1}{\Delta}$, which in the limit $\frac{\Delta}{E_F} >> 1$ would yield divergent contributions to the normalized (dimensionless) $\frac{\Delta}{J_b}\text{eff}\ w_{11}$. However, since Im $\bar{G}^{0\uparrow}_{00}$ and Im $G^{b\uparrow}_{00}$, integrated w.r.t the energy lead to n_s and n_b respectively, then there is an exact cancellation of these divergent terms in Eq (3.3.25). Such a cancellation occurs only if the HF corrections given by Eq (3.3.16) are included exactly. This shows that the HF corrections are essential in the surface spin-wave problem.

We are now able to express w^{itin}_{11}, calculated from Eq (3.3.25) in the Heisenberg-like form of Eq (3.2.17), ie

$$\frac{\Delta}{J_b}\text{eff}\ w^{\text{itin}}_{11} = w_o + w(q). \tag{3.3.29}$$

for a neutral surface ($n_s = n_b$). w_o can be identified with the constant (independent of $\underline{q}$) component of w^{itin}_{11} in Eq (3.2.17) and is given by

$$w_o = -1 - \left(\frac{n_b}{n_s}\right)\frac{1}{\pi n_b N} \sum_{\underline{k}} \int_{-\infty}^{E_F} (E - E_{\underline{q}} + E_o)\ \text{Im}\ \bar{G}^{0\uparrow}_{00}(\underline{k},E)dE \tag{3.3.30}$$

and hence the effective $\epsilon_{\perp}$ for an Itinerant ferromagnet is defined by

$$\epsilon_{\perp} = w_o + 2 \tag{3.3.31}$$

$w(\underline{q})$ comes from the terms in Eqs (3.3.26) and (3.3.27) containing $E_{\underline{q}}$ and can be expressed as $-4\,\Lambda\,(\underline{q})(1 - \epsilon_{||})$ with effective $\epsilon_{||}$ given by

$$\epsilon_{||} = -\left(\frac{n_b}{n_s}\right)^2 \frac{T}{\pi n_b N} \int_{-\infty}^{E_F} \sum_{\underline{k}} e^{i\underline{k}.\underline{R}_{n.n}} \,\mathrm{Im}\, G_{oo}^{-o\uparrow}(\underline{k},E)\, dE. \qquad (3.3.32)$$

Using Eq (3.3.31), we postulate that w_{12} and w_{22} for an Itinerant ferromagnet have the same form as the Heisenberg w_{12} and w_{22} in Eqs (3.2.12) and (3.2.13) respectively.

We now have an approximate w^{itin} which has the correct spin-rotational symmetry which will enable us to use it in Eq (3.3.20) and discuss the effect of surface on spin-waves. It is reasonable to choose w_{12} and w_{22} in this form since we can show that it is exact in the limit $\Delta/E_F \gg 1$. The proof is given in the next section.

3.4 The mapping of the Spin-Wave problem for a semi-infinite Metallic Ferromagnet onto an equivalent problem for an Insulator.

We showed in Sec. 3.3 that since the Itinerant surface perturbation is very much similar to that of a Heisenberg one, then it is reasonable to map one onto the other. We would now like to justify our mapping by showing that the value of $\epsilon_{\perp}$ deduced from W_{11}^{itin} given by Eq (3.3.31) is quite close to the true Itinerant $\epsilon_{\perp}$ which is defined by

$$\epsilon^{\mathrm{itin}} = \frac{J_{\perp}^{\mathrm{eff}}}{J_{\mathrm{bulk}}^{\mathrm{eff}}} \qquad (3.4.1)$$

Using Eq (2.5.11), we have

$$J_{\mathrm{bulk}}^{\mathrm{eff}} = U\Delta\bar{\Gamma}_{\mathrm{bulk}} \qquad (3.4.2)$$

and similarly

$$J_{\perp}^{\mathrm{eff}} = U\Delta\chi^{0} \qquad (3.4.3)$$

where $J_{\perp}^{\mathrm{eff}}$ is the effective exchange integral between spins in the surface (i=0) and its adjacent plane (i=1).

In the mixed Bloch-Wannier representation, Eq (3.4.1) is given by

$$\epsilon^{itin} = \frac{\sum_{\underline{q}_{||}} \chi^{o}_{o1}(\underline{q}_{||},\omega)}{\sum_{\underline{q}_{||}} \Gamma_{o1}(\underline{q}_{||},\omega)} \qquad (3.4.4)$$

with χ^{o}_{o1} given by Eq (3.3.12) and Γ_{o1} given by Eq (2.5.12). Hence, we require the one-electron HF propagators G^{-o}_{o1} and G^{b}_{o1}. Using the expansion (2.5.8) and keeping terms up to $(E_F/\Delta)^2$, we have in the limit $\Delta >> 1$,

$$\text{Re}\ G^{b\downarrow}_{o1}(E+\omega,\ \underline{k}+\underline{q}) = -\frac{T}{\Delta^2} \qquad (3.4.5)$$

and

$$\text{Re}\ G^{-o\downarrow}_{o1}(E+\omega,\ \underline{k}+\underline{q}) = -\frac{T}{\Delta^2}\left(\frac{n_b}{n_s}\right) \qquad (3.4.6)$$

With $\text{Im}\ G^{-o\uparrow}_{o1}$ and $\text{Im}\ G^{b\uparrow}_{o1}$ obtained from Eqs (3.3.15) and (2.5.1) respectively, we can now easily show that,

$$\epsilon^{itin} = \frac{n_b \int_{-\infty}^{E_F} -\frac{1}{\pi}\ \text{Im}\ G^{-o\uparrow}_{o1}\ dE}{n_s \int_{-\infty}^{E_F} -\frac{1}{\pi}\ \text{Im}\ G^{b\uparrow}_{o1}\ dE} .$$

$$= \epsilon_{\perp} \left(\frac{n_s}{n_b}\right) . \qquad (3.4.7)$$

For a neutral surface $(n_s = n_b)$, Eq (3.4.7) becomes

$$\epsilon^{itin} = \epsilon_{\perp} \qquad (3.4.8)$$

where $\epsilon_{\perp}$ is given by Eq (3.3.31)

We have thus proved that the surface problem for an Itinerant ferromagnet with $\frac{\Delta}{E_F} >> 1$, reduces exactly to a Heisenberg surface problem with $J^{eff}_{||}$ and $J^{eff}_{\perp}$ determined by the band structure.

Chapter 4 Magnetic Impurities in the Surface of Metallic Ferromagnets.

4.1 Introduction 4.

The magnetic properties of impurities on the surface of a metallic substrate are of interest and can now be studied experimentally when the number of impurity atoms amounts to a small fraction of an atomic layer. (See G Bergmann, 1979 ; G Allan ; 1984).

In this chapter, we wish to study the effect of an impurity atom in (and above) the surface of a ferromagnetic 3d metal. We approach this problem by studying their effective exchange integrals; which are as follows:-

(i) Effective exchange integral between an impurity atom buried in the surface and its nearest neighbouring atoms in the same plane.

(ii) Effective exchange integrals between an adatom and a metallic substrate atom just below it.

4.2 Surface Impurity Exchange Integrals in a Strong Tight-binding Itinerant Feromagnet.

There is, at the present time, a rapidly deepening insight into the behaviour of electrons in alloys. As systems with a continuously variable mean number of electrons per atom, alloys have always received a lot of attention from magnetic theorists and their properties have been rapidly invoked to support or oppose particular models. Although the inhomogeneity of a disordered alloy destroys the simple Bloch-wave character of the one-electron eigenfunctions of the many-electron system, it has been realised for sometime now that the electrons around an isolated atom in a sea of metallic electrons can be treated almost as satisfactorily as those of the host metal and that there are quite well-defined conditions for the occurrence on or near the impurity of an imbalance in the densities of up-and down-spin itinerant electrons, ie we may obtain a local moment. The effect of impurities on the spin-wave spectrum of bulk alloys has been studied, using a localized model. (See T Wolfram and J Callaway ; 1963).

The approach that we have undertaken here has already been described in Chapter 3. This model enables one to study the magnetic effect of impurities in metallic alloys. In this section, we are looking at the magnetic effect of one impurity atom buried in the surface-plane of a metallic substrate. The exchange coupling (or the indirect exchange) between the impurity atom and its nearest neighbouring host atom is taken to provide the necessary informations.

We begin by describing our substrate by a model for a strong tight-binding itinerant ferromagnet.

The model is one of electrons moving in a single band of Bloch-states with an interaction which operates only when two electrons of opposite spin are in Wannier-states on the same atom. (For this non-degenerate model, the ground-state for a completely ferromagnetic spin alignment is unaffected by the interaction). Thus, our substrate is a semi-infinite crystal, described by the one-band Hubbard model ; See Eq (1.2.1). The crystal itself is assumed to consist of $(N_{||} \times N_{\perp})$ atoms where $N_{||}$ is the number of atoms on a single layer parallel to the surface layer and $N_{\perp}$ is the number of layers. The layer is assigned by an index n, which is 0 for the top surface. Our Hubbard Hamiltonian is then given by

$$H^{imp} = H' + V^{imp} \tag{4.2.1}$$

where H' is the Hamiltonian of the semi-infinite pure substrate given by Eq(3.3.1) and V^{imp} is given by

$$V^{imp} = V_0^{imp} \sum_{\sigma} c_{0\sigma}^{*} c_{0\sigma} \tag{4.2.2}$$

with V_0^{imp} being the energy-level of the impurity atom. We now let $V_0^{imp\sigma}$ represent the HF surface impurity potential, ie

$$V_0^{imp\sigma} = V_0^{imp} + I_0^{eff} (\bar{n}_0^{imp\sigma} - \bar{n}_0^{\sigma}) \qquad (4.2.3)$$

where I_0^{eff} is the intra-atomic Coulomb interaction energy of the impurity atom. (Note that I_0^{eff} is assumed to be the same as in the substrate). n_0^{σ} and $n_0^{imp\sigma}$ are the number of σ-spin particles on the substrate atom and the impurity atom respectively.

It should be clear by now that the effective exchange integrals are derived from off-diagonal matrix-elements of their appropriate Green's functions. Thus, to obtain the effective exchange integral of an impurity atom buried in the surface plane of a substrate (as described above), we need to calculate the off-diagonal Green's function of the impurity. This can be derived using a Dyson Equation. However, we first set out to find the diagonal Green's function matrix-element at the impurity atom itself, since this is needed in the derivation of the off-diagonal Green's function. We hope that this will become clearer to the reader as we continue. We divide the work into two parts. In the first part, we derive the local Green's function of the impurity atom G_{00}^{imp} , and in the second part, the off-diagonal Green's function G_{01}^{imp} .

(I). The Diagonal Surface Impurity Green's Function.

We begin with the Dyson Equation

$$G^{imp\sigma} = G^{-0\sigma} + G^{-0\sigma} V_0^{imp\sigma} G^{imp\sigma} \qquad (4.2.4)$$

where $G^{imp\sigma}$ denotes the diagonal surface impurity Green's function; $G^{-0\sigma}$ is the diagonal surface Green's function of a pure substrate, derived in Appendix D and $V_0^{imp\sigma}$ is given by Eq (4.2.3).

Following the same approach described in Appendix D, it is easy to see that the local surface Green's function of the impurity atom, $G_{oo}^{imp\sigma}$ is then given by

$$G_{00}^{imp\sigma} = \frac{G_{00}^{-0\sigma}}{1 - G_{00}^{-0\sigma} V_0^{imp\sigma}} \qquad (4.2.5)$$

where $V_0^{imp\sigma}$ can be obtained self-consistently by Eq (4.2.3) with n_0^{σ} and $n_0^{imp\sigma}$ given by

$$n_0^{\sigma} = \frac{1}{\Pi} \int_{-\infty}^{E_F} \text{Im } G_{00}^{imp\sigma} (E) \; dE. \qquad (4.2.6)$$

$$n_0^{imp\sigma} = \frac{1}{\Pi} \int_{-\infty}^{E_F} \text{Im } G_{00}^{imp\sigma} (E) \; dE. \qquad (4.2.7)$$

Clearly, the presence of an impurity and hence a new surface Green's function G^{imp}, result in a new effective exchange integral $J^{eff}_{imp,||}$ compared with the old effective exchange integral J^{eff}; ie $J^{eff}_{imp,||}$ is taken to be the exchange coupling between the buried impurity atom in the surface and its nearest neighbouring atom also in the surface plane.

We now proceed to derive the off-diagonal Green's function in order to obtain $J^{eff}_{imp,||}$.

(II) The Off-diagonal Surface Impurity Green's Function.

We let $\underline{R}_{||}$ denote the position-vector between the impurity atom and its nearest neighbouring atom in the surface plane, ie

$$\underline{R}_{||} = (0 \quad a) \tag{4.2.8}$$

The off-diagonal Green's function of the impurity atom can then be derived using Eq (D21) (See Appendix D), where in place of the surface Green's functions of the pure substrate ie $G^{0\sigma}_{01}$ and $G^{0\sigma}_{00}$, we must now substitute $G^{-0\sigma}_{01}$ and $G^{-0\sigma}_{00}$ respectively. Also, the corresponding potential $V^{imp\sigma}_{0}$ replaces V^{σ}_{0}. Thus, we have

$$G^{imp\sigma}_{01} = \frac{G^{-0\sigma}_{01}}{1 - G^{-0\sigma}_{00} V^{imp\sigma}_{0}} \tag{4.2.9}$$

As in Chapter 3, the susceptibility of this system will now determine the surface impurity effective exchange integral $J_{imp,||}^{eff}$. It follows from Eq (3.3.12) that the off-diagonal surface impurity susceptibility of a strong ferromagnet can now be evaluated by

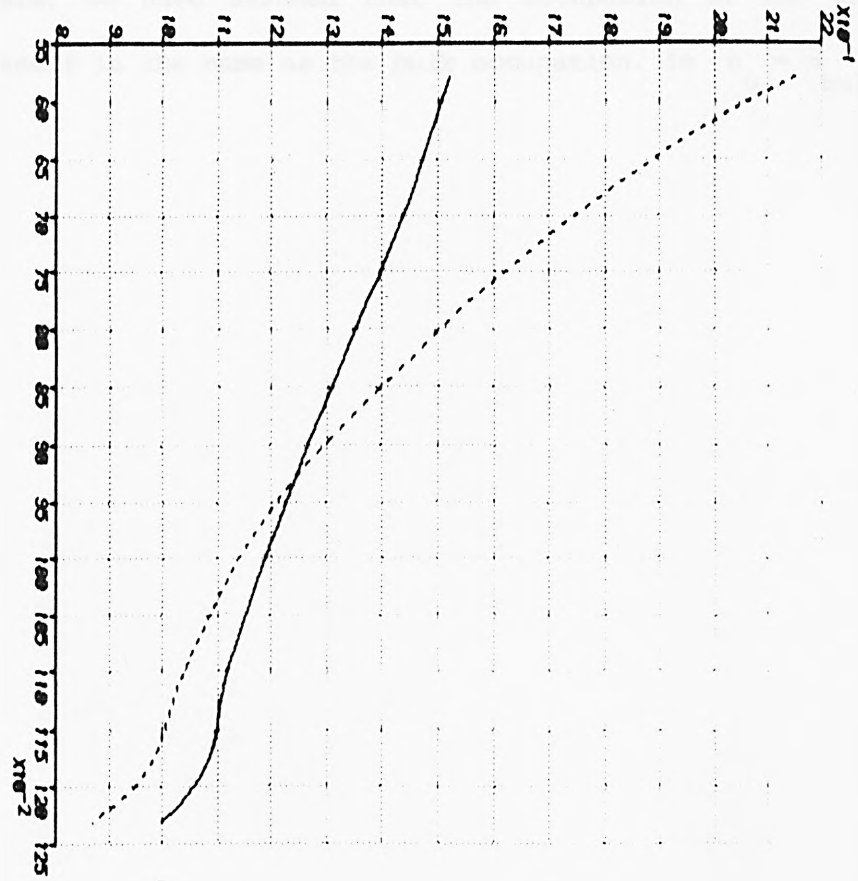
$$\chi_{01}^{imp,||}(\omega) = -\frac{1}{\Pi}\int_{-\infty}^{E_F} \mathrm{Re}\, G_{01}^{imp\downarrow}(\omega + E)\, \mathrm{Im}\, G_{01}^{imp\uparrow}(E)\, dE. \tag{4.2.10}$$

and by Eq (2.5.11), we then have

$$J_{imp,||}^{eff} = U\Delta\chi_{01}^{imp,||} \tag{4.2.11}$$

It is of interest to show first the surface effective exchange integral in the absence of an impurity.

Fig 1(a) shows the dependence of the surface effective exchange integral $J_{||}^{eff} / J_{bulk,||}^{eff}$ (normalised on the occupation of the surface layer n_0/n_{bulk}. Solid curve is for $n_{bulk} = 0.2$ and $\Delta/E_F = 2$; broken curve is for $n_{bulk} = 0.2$ and $\Delta/E_F >> 1$.



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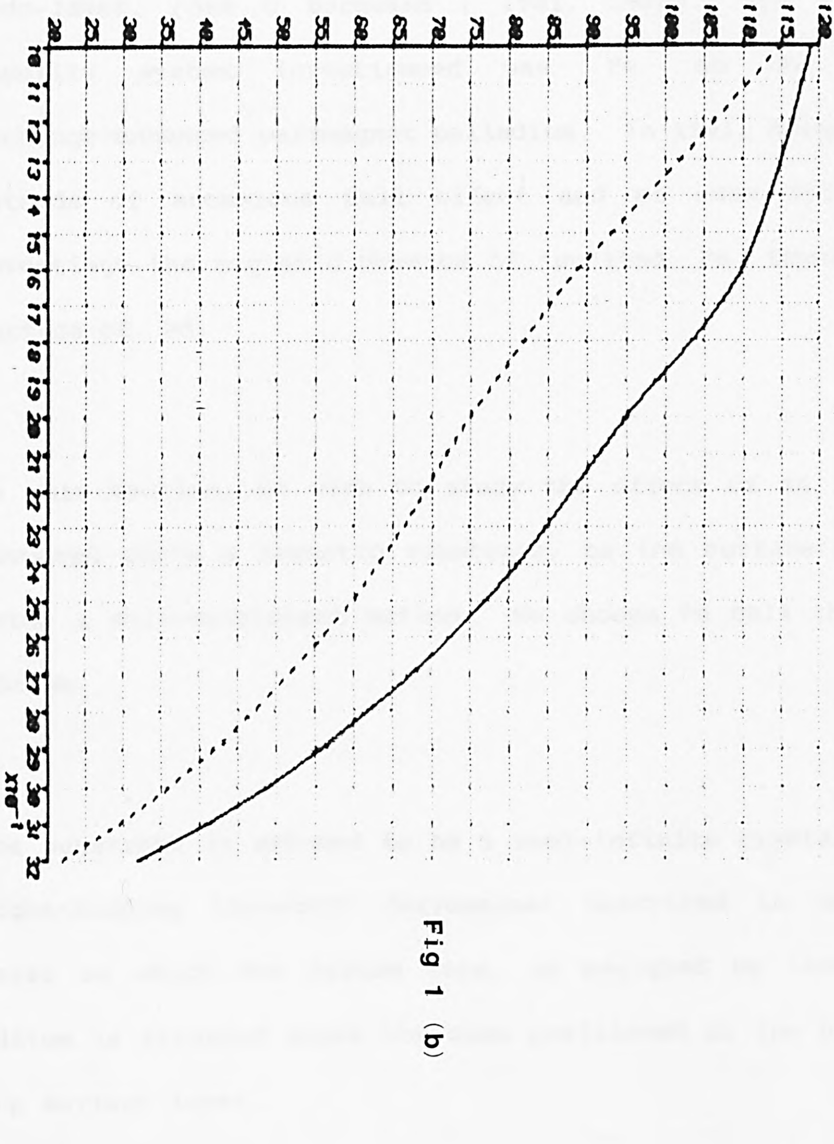
x10^-2

Fig 1 (a)

Fig 1(b) shows the dependence of the surface impurity effective exchange integral $J^{eff}_{imp,||}/J^{eff}_{bulk.||}$ on the occupation of the surface impurity n^{imp}_{0}/n_{bulk} . Solid curve is for $n_{bulk} = 0.2$ and $\Delta/E_F = 2$; broken curve is for $n_{bulk} = 0.2$ and $\Delta/E_F \gg 1$. Here, we have assumed that the occupation of the surface layer itself is the same as the bulk occupation, ie $n_0 = n_{bulk}$.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x10^-1

Fig 1 (b)

4.3 Magnetic Effects of An Impurity Atom Above The Surface of A Strong Itinerant Ferromagnet.

The magnetic moment of impurities on the surfaces of metals can now be measured down to concentrations of a few per cent of a mono-layer. (See G Bergmann ; 1981, 1982). The first surface impurity system investigated was Fe on the surface of exchange-enhanced paramagnet palladium. In 1981, Bergmann used the methods of anomalous Hall effect and of weak localization to investiage the magnetic moments of isolated Fe impurities on the surface of Pd.

In this section, we wish to study the effect of an impurity atom situated above a magnetic substrate, on the surface magnetization using a self-consistent method. We choose to call this atom, the adatom.

The substrate is assumed to be a semi-infinite crystal of a strong tight-binding itinerant ferromagnet described in Sec 4.2. The layer on which the adatom lies, is assigned by index 1 and the adatom is situated above the atom positioned at the origin, on the top surface layer.

It is easy to see that the presence of such an atom (adatom) will affect the surface charge density in its immediate vicinity. This means that the surface charge neutrality that is enforced by the HF potential V_0^{σ} given by Eq (3.3.16) is then lost. In other words, the number of electrons on the surface atom, below the adatom is no longer equal to its bulk value, i.e $n_0 \neq n_b$. However, this problem can be overcome by introducing an adjustable potential for the surface atom. This potential could be interpreted as having an impurity atom buried in place of the pure surface atom. This idea is based on the fact that the presence of such an atom results in a perturbation which is then modelled by a new potential (as discussed in Sec 4.2).

It is now justified to describe our system by the Hubbard Hamiltonian

$$H^{ad} = H^{imp} + V^{ad} \tag{4.3.1}$$

where H^{imp} is the Hamiltonian of the semi-infinite crystal with an "impurity" buried in the surface. H^{imp} is then given by Eq (4.2.1), and V^{ad} is given by

$$V^{ad} = \sum_{i,\sigma} T_{i1}(c^{*}_{i\sigma}\, c_{1\sigma} + c^{*}_{1\sigma}\, c_{i\sigma}) \tag{4.3.2}$$

with T_{i1} representing the hopping integrals for the electronic transition between the adatom and the substrate which may be different from E_{ij}.

Using the Hamiltonian H^{ad}, we can now find the local Green's function $G^{ad\sigma}_{11}$ of the adatom, by solving the Dyson Equation

$$G^{ad\sigma} = G^{imp\sigma} + G^{imp\sigma} V^{ad\sigma} G^{ad\sigma} \qquad (4.3.3)$$

where $G^{imp\sigma}$ is given by Eq (4.2.5).

However, it should be noted that the HF impurity potential $V_0^{imp\sigma}$ (See Eq (4.2.3)) depends on the occupation of the "impurity" atom, and this, must be determined by taking into account the effect of the adatom on the "impurity" atom. This is discussed in detail in Sec 4.3.1.

Thus, we have

$$G^{ad\sigma}_{mn} = G^{imp\sigma}_{mn} + \sum_{p,q} G^{imp\sigma}_{mp} V^{ad\sigma}_{pq} G^{ad\sigma}_{qn} \qquad (4.3.4)$$

By defining

$$V^{ad\sigma}_{pq} = \begin{cases} V^{ad\sigma}_{1} & p = q = 1 \\ T & p = 0,\ q = 1 \text{ and } p = 1,\ q = 0 \\ 0 & \text{otherwise.} \end{cases} \qquad (4.3.5)$$

Then Eq (4.3.4) is simplified to

$$G^{ad\sigma}_{mn} = G^{imp\sigma}_{mn} + G^{imp\sigma}_{m1}\left(V^{ad\sigma}_{1}\, G^{ad\sigma}_{1n} + T\, G^{ad\sigma}_{0n}\right) + G^{imp\sigma}_{m0}\, T\, G^{ad\sigma}_{1n} \ . \qquad (4.3.6)$$

The local Green's function $G^{ad\sigma}_{11}$ is then obtained by putting $m = n = 1$ in Eq (4.3.6) ie

$$G^{ad\sigma}_{11} = G^{imp\sigma}_{11} + G^{imp\sigma}_{11}\left(V^{ad\sigma}_{1}\, G^{ad\sigma}_{11} + T\, G^{ad\sigma}_{01}\right) + G^{imp\sigma}_{10}\, T\, G^{ad\sigma}_{11}$$

$$= (E^{\sigma})^{-1} + (E^{\sigma})^{-1}\left(V^{ad\sigma}_{1}\, G^{ad\sigma}_{11} + T\, G^{ad\sigma}_{01}\right) \qquad (4.3.7)$$

where

$$G^{imp\sigma}_{11} = (E^{\sigma})^{-1} \qquad (4.3.8)$$

$$G^{imp\sigma}_{10} = G^{imp\sigma}_{01} = 0 \qquad (4.3.9)$$

and E_{σ} is given by Eq (1.3.62).

To find $G^{ad\sigma}_{01}$, we put $m = 0$, $n = 1$ in Eq (4.3.6) which would then give

$$G^{ad\sigma}_{01} = G^{imp\sigma}_{00} \; T \; G^{ad\sigma}_{11} \qquad (4.3.10)$$

substituting Eq (4.3.10) into Eq (4.3.7) , we get

$$G^{ad\sigma}_{11} = (E^{\sigma})^{-1} + (E^{\sigma})^{-1} (V^{ad\sigma}_{1} \; G^{ad\sigma}_{11} + G^{imp\sigma}_{00} \; T^{2} \; G^{ad\sigma}_{11})$$

which simplifies to

$$G^{ad\sigma}_{11} = (E^{\sigma} - V^{ad\sigma}_{1} - T^{2} \; G^{imp\sigma}_{00})^{-1} \qquad (4.3.11)$$

The off-diagonal Green's function of the adatom, ie $G^{ad\sigma}_{01}$, is then obtained by substituting Eq (4.3.11) into Eq (4.3.10):

$$G^{ad\sigma}_{01} = T \; G^{imp\sigma}_{00} \; (E^{\sigma} - V^{ad\sigma} - T^{2} \; G^{imp\sigma}_{00})^{-1} \qquad (4.3.12)$$

where $V^{ad\sigma}_{1}$ is the HF level of the adatom, given by

$$V^{ad\sigma}_{1} = V_{1} + I^{eff}_{1} \; n^{ad\bar{\sigma}}_{1} \qquad (4.3.13)$$

T is the hopping integral between the adatom and the substrate, (both V_1 and T are adjustable parameters) ; $n_1^{ad\sigma}$ is the number of σ-spin particles on the adatom, given by

$$n_1^{ad\sigma} = \frac{1}{\Pi} \int_{-\infty}^{E_F} \text{Im}\, G_{11}^{ad\sigma}(E)\, dE. \qquad (4.3.14)$$

The off-diagonal Green's function $G_{01}^{ad\sigma}$ given by Eq (4.3.12) can be used to determine the effective exchange-integral $J_{ad,\perp}^{eff}$ between the adatom and an impurity on the surface of a strong ferromagnetic metal. It follows from Eq (3.2.12) that $J_{ad,\perp}^{eff}$ can be determined by the off-diagonal susceptibility matrix-element given by

$$\chi_{01}^{ad,\perp}(\omega) = -\frac{1}{\Pi} \int_{-\infty}^{E_F} \text{Re}\, G_{01}^{ad\downarrow}(\omega + E)\, \text{Im}\, G_{01}^{ad\uparrow}(E)\, dE \qquad (4.3.15)$$

Thus, $J_{ad,\perp}^{eff}$ is then determined by

$$J_{ad,\perp}^{eff} = U \Delta \chi_{01}^{ad,\perp} \qquad (4.3.16)$$

Fig 2(a) shows the dependence of the adatom effective exchange integral $J_{ad,\perp}^{eff}/J_{bulk,\perp}^{eff}$ (with a Ni surface) on the occupation of the adatom n_1^{ad}/n_{bulk}. Solid curve is for $n_{bulk} = 0.2$ and $\Delta/E_F = 2$; broken curve is for $n_{bulk} = 0.2$ and $\Delta/E_F \gg 1$. Here, we have assumed that the occupation of the surface impurity is the same as the bulk occupation, ie $n_o^{imp} = n_{bulk}$.

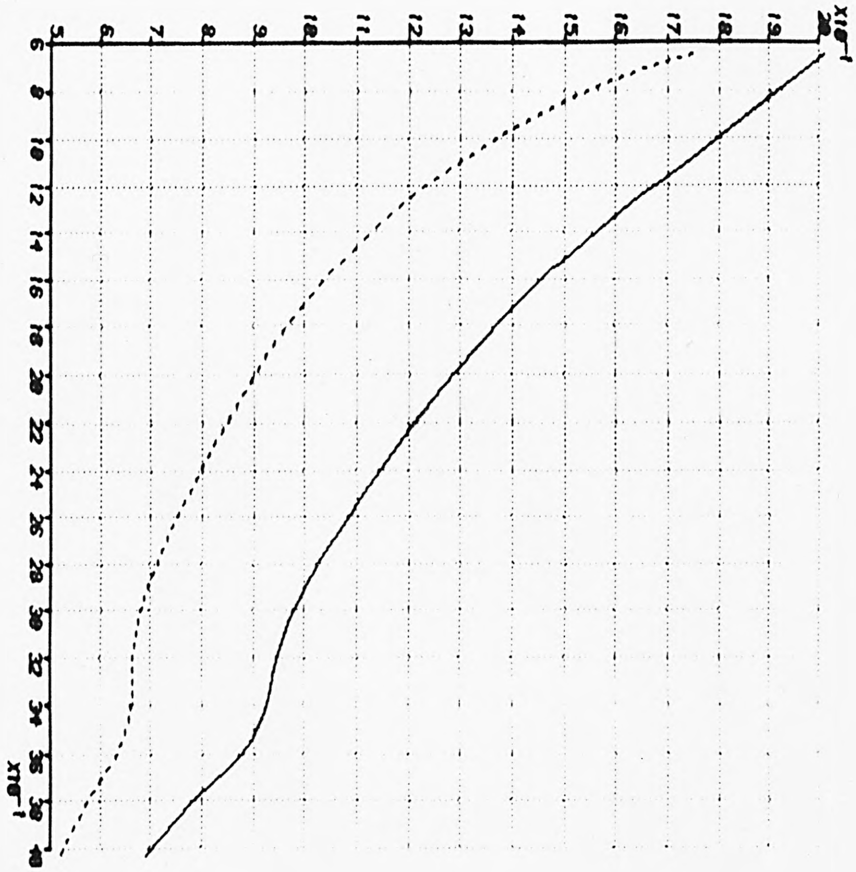
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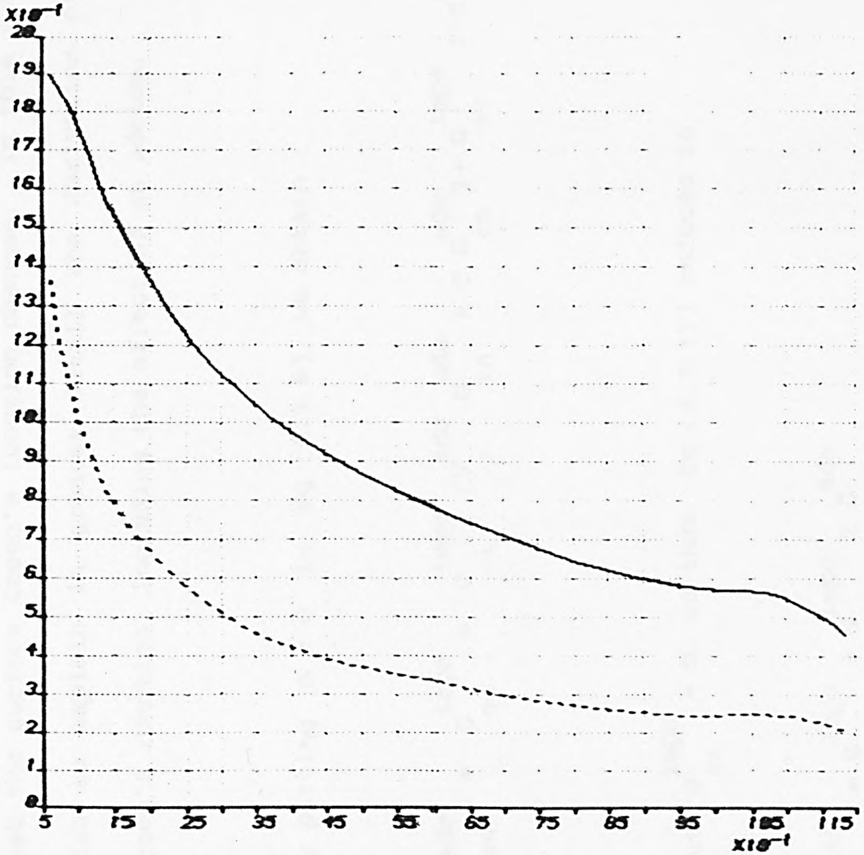
Fig 2 (a)

Fig 2(b) shows the dependence of the adatom effective exchange integral $J^{eff}_{ad,\perp}/J^{eff}_{bulk,\perp}$ (with a Pd surface) on the occupation of the adatom n^{ad}_{1}/n_{bulk}. Solid curve is for $n_{bulk} = 0.07$ and $\Delta/E_F = 2$; broken curve is for $n_{bulk} = 0.07$ and $\Delta/E_F >> 1$. Again, we have assumed that $n^{imp}_{o} = n_{bulk}$.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x10^-1

Fig 2 (b)

4.3.1 The Effect of An Adatom On The Surface Green's Function.

We discussed in the earlier part of Sec 4.3, that the presence of an adatom positioned above the surface of a metallic substrate will affect the surface charge neutrality. This would then indicate that the surface Green's function changes. In this subsection, we wish to explain in greater detail the derivation of a surface Green's function, including the effect of an adatom.

By putting $m = 0$ in Eq (4.3.6), we obtain

$$G_{on}^{ad\sigma} = G_{on}^{imp\sigma} + G_{o1}^{imp\sigma}\left(V_1^{ad\sigma} G_{1n}^{ad\sigma} + T G_{on}^{ad\sigma}\right) + G_{oo}^{imp\sigma} T G_{1n}^{ad\sigma} \tag{4.3.17}$$

But $G_{o1}^{imp\sigma} = 0$, so that Eq (4.3.17) reduces to

$$G_{on}^{ad\sigma} = G_{on}^{imp\sigma} + G_{oo}^{imp\sigma} T G_{1n}^{ad\sigma} \tag{4.3.18}$$

Putting $n = 0$, we get

$$G_{oo}^{ad\sigma} = G_{oo}^{imp\sigma} + G_{oo}^{imp\sigma} T G_{1o}^{ad\sigma} \tag{4.3.19}$$

Substituting Eq (4.3.12) in Eq (4.3.19), we find that

$$G_{oo}^{ad\sigma} = \frac{E^{\sigma} - V_{1}^{ad\sigma} \quad G_{oo}^{imp\sigma}}{E^{\sigma} - V_{1}^{ad\sigma} - T^{2} G_{oo}^{imp\sigma}} = G_{oo}^{imp,ad\sigma} \quad . \qquad (4.3.20)$$

(To be consistent with our notation, we choose to replace $G_{oo}^{ad\sigma}$ by $G_{oo}^{imp,ad\sigma}$).

$G_{oo}^{imp,ad\sigma}$ is then the new surface Green's function, with $G_{oo}^{imp\sigma}$ and $V_{1}^{ad\sigma}$ given by Eqs (4.2.5) and (4.3.5) respectively.

The number of particles on the surface atom, is now evaluated using the appropriate Green's function $G_{oo}^{imp,ad\sigma}$, ie

$$n_{o}^{imp,ad\sigma} = \frac{1}{\Pi} \int_{-\infty}^{E_F} G_{oo}^{imp,ad\sigma}(E) \;\; dE. \qquad (4.3.21)$$

It is important to note that in the calculation of $G_{11}^{ad\sigma}$ and $G_{o1}^{ad\sigma}$ the surface Green's function $G_{oo}^{imp\sigma}$ given by Eq (4.2.6), should have its HF potential $V_{o}^{imp\sigma}$ (See Eq (4.2.3)) replaced by

$$V_{o}^{imp} = V_{o}^{imp} + I_{o}^{eff}(n^{imp,ad\bar{\sigma}} - n_{o}^{imp\bar{\sigma}}) \qquad (4.3.22)$$

4.4 Up-Spin Localized (bound) States Outside The Energy-Band.

From Figs 2(a) and (b), it can be seen that $J^{eff}_{ad,\perp}$ decreases with increasing occupation of the adatom, ie with increasing attractive potential on the adatom. This seems to suggest that $J^{eff}_{ad,\perp}$ might become zero for some critical values of $V^{ad\sigma}_{1}$ and T. This would imply loss of stability of the ferromagnetic ground-state of the adatom. Since, we are considering a strong ferromagnet, then this can only happen if a $\downarrow$-spin bound-state is formed. (For a strong ferromagnet, there exists no $\downarrow$-spin extended states in the band). Therefore, it is necessary to investigate the range of $V^{ad\uparrow}_{1}$, T for which such a bound-state can occur. This is the subject of this section.

For a strong ferromagnet, the exchange-splitting Δ is such that only states of $\uparrow$-spin direction lie below the Fermi-level. For a spatially inhomogeneous ferromagnet, the $\uparrow$-spin states may be of two types: band (extended) state and bound (localized) states. The localized states have isolated energy-levels that lie outside the bulk spectrum. These isolated energy-levels are the poles of the Green's function that describes the system. We, therefore, start with the ad-atom Green's function $G^{ad\uparrow}_{11}$ (See Eq (4.3.11)) to show how and when these bound-states occur. (In the following section, we shall show that the stability of ferromagnetic states depends very much on the existence of such bound-states).

Consider the Green's function of the ↑-spin states of an impurity atom above a strong semi-infinite ferromagnetic substrate, ie

$$G_{11}^{ad\uparrow} = \left[E - V_{1}^{ad\uparrow} - T^{z} G_{oo}^{imp\uparrow}(E)\right]^{-1} \tag{4.4.1}$$

(See Eq (4.3.11)).

It can be readily seen that the poles of $G_{11}^{ad\uparrow}$, outside the bulk continuum, exist if

$$E - V_{1}^{ad\uparrow} - T^{z} \operatorname{Re} G_{oo}^{imp\uparrow}(E) = 0 \tag{4.4.2}$$

for $|E| < E_{\underline{k}}$.

The fact that the energy spectrum is obtained from the imaginary part of the Green's function only, (See Sec 1.3.4) suggests that outside the band Im G = 0. Hence, outside the energy-band $G_{oo}^{imp\uparrow} = \operatorname{Re} G_{oo}^{imp\uparrow}$ in Eq (4.4.2).

Eq (4.4.2) can be rewritten as

$$E_{b}^{\uparrow} = V_{1}^{ad\uparrow} - T^{z} \operatorname{Re} G_{oo}^{imp\uparrow}(E = E_{b}^{\uparrow}). \tag{4.4.3}$$

where $E_{b}^{\uparrow}$ is the energy-level of the ↑-spin state which lies outside the ↑-spin band.

It is useful to note that since the local Green's function $G_{oo}^{imp,ad\uparrow}$ of the substrate (See Eq (4.3.20)) has also the same denominator as $G_{11}^{ad\uparrow}$ of the adatom, then the surface substrate atom will also have a bound-state with the same atomic energy-level $E_b^{\uparrow}$ given by Eq (4.4.3).

From Eq (4.3.13) and since there are no $\downarrow$-spin particles, ie $n_1^{ad\downarrow} = 0$, we deduce

$$V_1^{ad\uparrow} = V_1 \tag{4.4.4}$$

To obtain the range of V_1, T for which such bound-states exists, Eq (4.4.3) has to be solved numerically.

4.4.1 The Occupation-Number of The Up-Spin Bound-State

In general, we might find two, one or no localized states depending on the hopping integral T and on the value of V_1, ie we might have a situation where there is :-

a) One bound-state above the energy-band AND one below it;

b) One bound-state EITHER above OR below the band;

c) NO bound-states.

In the present context, only the bound-state below the band is relevant, since the bound-state above the band would be unoccupied.

It is clear that in (a) and (b), the number of particles inside the band decreases, since some would have to fill the energy-band of the bound-state(s). The range of V_1, T for which a bound-state below the band occurs is shown in Fig 3.

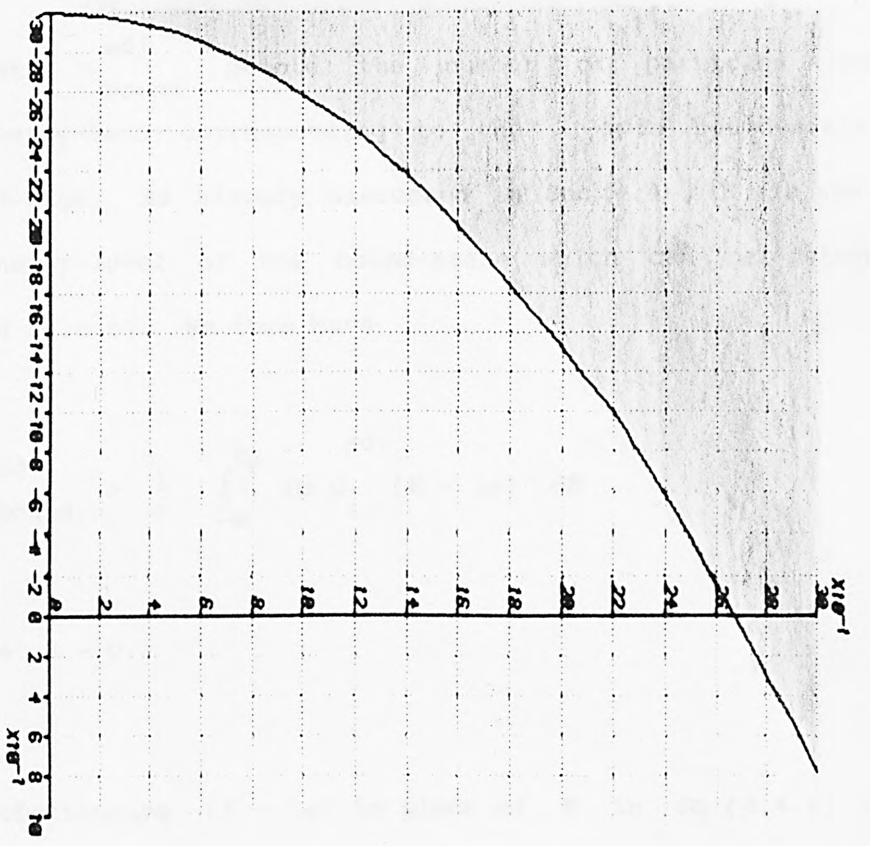
-30 -28 -26 -24 -22 -20 -18 -16 -14 -12 -10 -8 -6 -4 -2 0 2 4 6 8 10
x10^-1
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
x10^-1

Fig 3

In this section, we shall show how the number of particles inside a bound-state is calculated and as in the previous section we choose to work with $G_{11}^{ad\uparrow}$.

Let $n_{bound}^{ad\uparrow}$ denote the number of particles inside the energy-band corresponding to the $\uparrow$-spin bound-state of the ad-atom. As already discussed in Sec 4.4 , $E_b^{\uparrow}$ is the atomic energy-level of the bound-state which can be determined by Eq (4.4.3). We then have

$$n_{bound}^{ad\uparrow} = \frac{1}{\pi} \int_{-\infty}^{E_F} \operatorname{Im} G_{11}^{ad\uparrow} (E - i\epsilon) \; dE \qquad (4.4.5)$$

as $\epsilon \to 0$.

Substituting $(E - i\epsilon)$ in place of E in Eq (4.4.1) and using Eq (4.4.4), we have

$$G_{11}^{ad\uparrow} (E - i\epsilon) = E - \epsilon - V_1 - T^2 \operatorname{Re} G_{00}^{imp\uparrow} (E - i\epsilon) \qquad (4.4.6)$$

$$= \frac{E - V_1 - T^2 \operatorname{Re} G_{00}^{imp\uparrow} (E - i\epsilon) + i\epsilon}{[E - V_1 - T^2 \operatorname{Re} G_{00}^{imp\uparrow} (E - i\epsilon)]^2 + \epsilon^2} \qquad (4.4.7)$$

From Eq (4.4.7), we can deduce

$$\operatorname{Im} G_{11}^{ad\uparrow} (E - i\epsilon) = \frac{\epsilon}{[E - V_1 - T^2 \operatorname{Re} G_{00}^{imp\uparrow} (E - i\epsilon)]^2 + \epsilon^2} \qquad (4.4.8)$$

As $\epsilon \to 0$, multiplying Eq (4.4.8) by $\frac{1}{\pi}$, we get a delta-function of the form

$$\frac{1}{\pi} \operatorname{Im} G_{11}^{ad\uparrow}(E) = \delta[E - \{V_1 + T^2 \operatorname{Re} G_{oo}^{imp\uparrow}(E)\}] \tag{4.4.9}$$

Substituting Eq (4.4.9) into Eq (4.4.5), we have

$$n_{bound}^{ad\uparrow} = \int_{-\infty}^{E_F} \delta[E - \{V_1 + T^2 \operatorname{Re} G_{oo}^{imp\uparrow}(E)\}] \; dE \tag{4.4.10}$$

which can be written in the form

$$n_{bound}^{ad\uparrow}(E_b^{\uparrow}) = \int \frac{\delta(t)}{1 - T^2 \frac{d}{dE}\{\operatorname{Re} G_{oo}^{imp\uparrow}(E)\}\Big|_{E = E_b^{\uparrow}}} \; dt. \tag{4.4.11}$$

where

$$t = E - V_1 - T^2 \operatorname{Re} G_{oo}^{imp\uparrow}(E) \tag{4.4.12}$$

Using $\int \delta(t) = 1$, Eq (4.4.11) reduces to

$$n_{bound}^{ad\uparrow}(E_b^{\uparrow}) = \frac{1}{1 - T^2 \frac{d}{dE}\{\operatorname{Re} G_{oo}^{imp\uparrow}(E)\}\Big|_{E = E_b^{\uparrow}}} \tag{4.4.13}$$

which gives the occupation number of particles in the $\uparrow$-spin bound at $E_b^{\uparrow}$.

Similarly, one can obtain the occupation number of particles, $n_{bound}^{imp,ad\uparrow}$ namely, in the $\uparrow$-spin bound-state band of the surface impurity atom. It follows that by considering the Green's function $G_{oo}^{imp,ad\uparrow}$ (See Eq 4.3.20) we get

$$n_{bound}^{imp,ad\uparrow}(E_b^{\uparrow}) = T^2[\mathrm{Re}\, G_{oo}^{imp\uparrow}(E_b^{\uparrow})]^2\, n_{bound}^{ad\uparrow}(E_b^{\uparrow}) \qquad (4.4.14)$$

where $n_{bound}^{ad\uparrow}$ is given by Eq (4.4.13).

4.5 Instability of Magnetic Surface Impurity.

Bergmann (1981,1982) used the methods of anomalous Hall effect and of weak localization to investigate the magnetic moments of Fe impurities on the surfaces of polyvalent metals and on the surface of Pd. He found that Fe impurities on such surfaces show stronger tendency toward moment formation than in the bulk. This can be explained within the Anderson model. A surface impurity has fewer neighbours than in the bulk, the impurity level is narrower and therefore, the local Stoner condition for magnetic moment is easier to satisfy on the surface than in the bulk. This already happens for an impurity burried in the surface. A tight-binding calculation of the local susceptibility of a surface impurity confirms this qualitative argument. (See J Mathon ; 1983).

However, there is one important exception to this rule. A bulk Fe impurity has a giant moment of about $10\mu_B$ in Pd, but Bergmann found no moment for an Fe adatom on the surface of Pd. It has been shown by Bergmann and Mathon (1986) and also Gradmann and Bergholz (1984) that measurements on Pd-Ni-Pd and Ni-Pd sandwiches indicate that the surface susceptibility of Pd is at least as high as in the bulk.

It is only reasonable to expect that an Fe impurity on the surface of Pd should also induce a giant moment at least as large as in the bulk. One possible explanation for the absence of moment is that the ferromagnetic state of a surface impurity is less stable than that in the bulk, ie it becomes unstable and therefore the total moment reduces. To demonstrate this, we use an argument analogous to that of Friedel and Kanamori, (See J Friedel ; 1958 - J Kanamori, 1965). We shall show that the adatom impurity potential for Fe in Pd is strong enough in the surface to produce a localized state in the $\downarrow$-spin band, but is nonetheless weaker than that in the bulk. To show this, we need consider the $\downarrow$-spin local Green's function of the adatom, ie

$$G^{ad\downarrow}_{1,1} = (E - V^{\downarrow}_{1} - T^{2} G^{imp\downarrow}_{oo})^{-1} \qquad (4.5.1)$$

and show that for some values of the hopping integral T and the adatom potential V_1, the condition for a bound-state, ie

$$E' - V^{\downarrow}_{1} - T^{2} \, \mathrm{Re} \, G^{imp\downarrow}_{oo}(E') = 0 \qquad (4.5.2)$$

is satisfied at the bottom of the $\downarrow$-spin band, where

$$E' = E + \Delta. \qquad (4.5.3)$$

Δ is the substrate exchange splitting.

Using Eq (4.2.4), we have

$$V^{\downarrow}_{1} = V_{1} + I^{eff}_{1} n^{ad\downarrow}_{1} . \qquad (4.5.4)$$

To solve this self-consistent problem, we have used a semi-elliptical model density of states for the surface atomic layer. In Fig 4, the dependencies of the adatom occupation n_1^{ad} on the adatom potential V_1 are shown for two values of adatom/surface hopping T.

Since Bergmann (1981) estimated that Fe impurities in his experiment interacted with about six substrate atoms, we chose the values of T to be about half of the substrate bandwidth. This is consistent with the impurity having six nearest neighbours rather than twelve, as it would have in the bulk.

The arrows in Fig 4 indicate where the transition from the ferromagnetic onto the antiferromagnetic state occurs. It happens in our one-band model for $n_1^{ad} \simeq 0.8 - 0.9$, depending on the precise value of T. This value is consistent with the number of holes on a free Fe atom, ie 4. The instability of the ferromagnetic state of a surface impurity obtained here, could be the explanation of Bergmann's results. It is interesting to note that such an instability occurs only if the occupation of the adatom is large. This would not happen for Ni adatom and this agrees with unpublished results of Bergmann, which show that Ni atoms have a moment on the surface of Pd.

Our results can also be compared with those obtained by Lopez and Falicov (1982). However, they only considered the limit when the occupation of the adatom is large, ie the case of antiferromagnetic coupling. They did not discuss the transition between ferro and anti-ferromagnetic state which we have done.

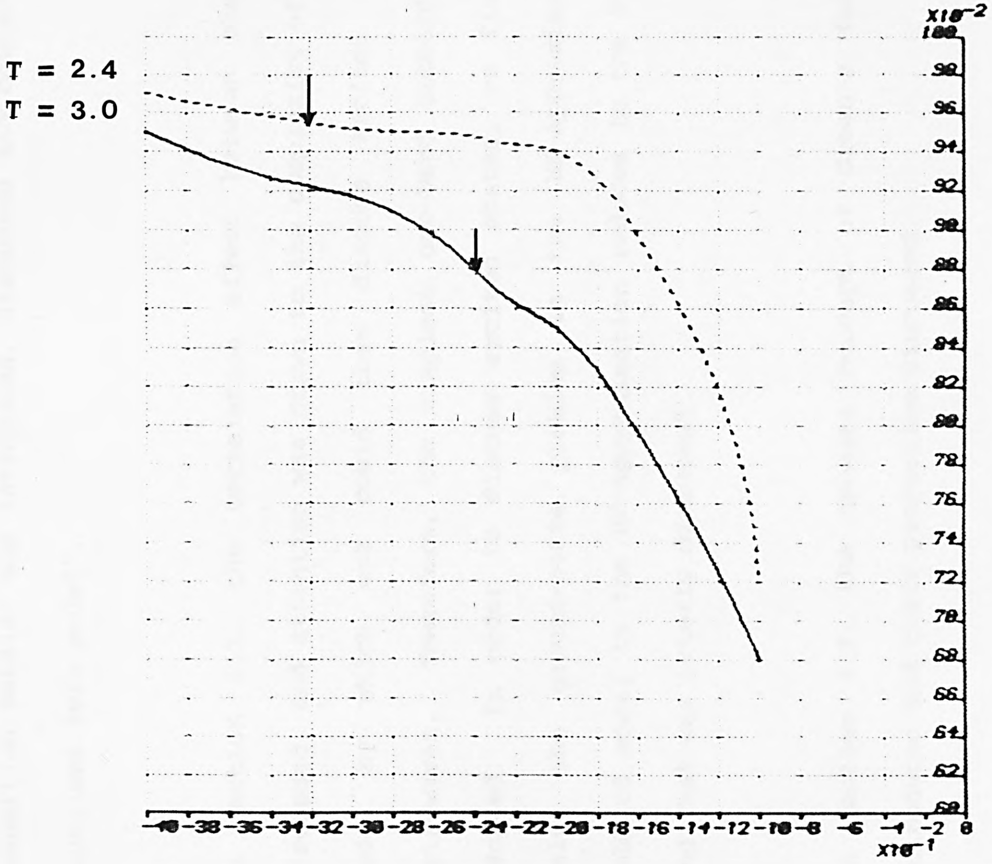
T = 2.4
T = 3.0
x10^-2
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
64
62
60
-40 -38 -36 -34 -32 -30 -28 -26 -24 -22 -20 -18 -16 -14 -12 -10 -8 -6 -4 -2 0
x10^-1

Fig 4

CONCLUSION

In section 1.1, the 'Itinerant model of ferromagnetism of transition metals' was introduced, discussed and compared with the Localized spin model'.

In section 1.2, the correlation effect between electrons was discussed, and attention was drawn to the complexity of deriving a model by which one could then discuss excited states, ie spin-waves. Therefore, the simplest one-band Hubbard model was adopted. In order to discuss excited states, we first have to solve the ground-state problem in the HF-approximation. The Hubbard model in the HF-approximation reduces to the Stoner model and that was briefly discussed.

In section 1.3, the general concept of Green's functions was introduced and their properties discussed.

In section 2.1, the Heisenberg model is described, since this is widely used in determining spin-waves in magnetic insulators. More importantly, it became the basis of our work in deriving an effective Heisenberg ferromagnet, using the band-theory.

In section 2.2, a review of the properties of the bulk spin-waves in a Heisenberg ferromagnet was presented. It was deduced that the Transverse susceptibility of such a system was directly related to the Green's function of Heisenberg Hamiltonian.

In section 2.3, the Transverse Dynamical susceptibility of an Itinerant ferromagnet was presented, whose poles give the spin-wave energies in the bulk of such ferromagnets. It was shown that these poles lead to two types of excitation energies : the Stoner energies which form a continuum and isolated energies known as the bulk spin-wave energies.

In section 2.4, the results of the previous section 2.2 and 2.3 were used to give some physical insight into the properties of spin-waves in Itinerant ferromagnet. This was achieved by showing that the Itinerant spin-wave Green's function in the Wannier representation had the same form as the Heisenberg Green's function. When compared, the exchange integrals were found to be proportional to the transverse static unenhanced susceptibility in the HF approximation of the Itinerant ferromagnet. Thus, a simple physical interpretation could be given to such susceptibilities. The bulk effective exchange integrals were computed from the one-electron HF-propagators. This procedure is referred to as 'mapping an Itinerant ferromagnet onto an effective Heisenberg one', where the exchange integrals were determined by using the one-band Hubbard model. A further advantage of such an effective J is that we could use the results of Wolfram and Callaway (1963) to interpret the effect of an isolated impurity on the spin-waves in the bulk of an Itinerant ferromagnet.

In section 2.5, it was proved that the effective exchange integrals were of appreciable size only for distances of the order of electron hopping. The one-band Hubbard model we have used included only nearest neighbouring electron interactions. It was then argued that only the effective exchange integrals of nearest neighour coupling were important.

In section 3.1, surface spin-waves were introduced. It was pointed out that the surface magnetization at finite temperatures in both metallic and non-metallic ferromagnets is determined by such spin-waves. The aim of this chapter was to use the results of Chapter 2, in order to study the spin-wave problems for a semi-infinite metallic ferromagnet with impurities on its surface-plane.

In section 3.2, a brief account was given of the results obtained by De Wames and Wolfram (1969), on the effect of surface on non-metallic ferromagnets. It was shown that the effect of surface can be described in two stages. In the first stage, all bulk exchange integrals are set equal to zero across the surface. This was referred to as the 'Geometric effect of the surface.' In the second stage, the surface exchange was renormalized by computing the exchange integrals in the surface plane and in the plane immediately adjacent to it. These were determined by calculating the perturbation matrix W^{Heis} from a Dyson equation.

In section 3.3, the surface spin-waves problem for a semi-infinite metallic ferromagnet was formulated by adopting the same approach for an equivalent problem for an insulator, (discused in the previous section). Our approach is a substantial improvement on the CIBM of Griffin and Gumbs (1976). This is due to two main factors: firstly, we worked in real-space where the surface perturbation is of short-range, whereas the surface perturbation in CIBM is of long-range since they worked in the $\underline{k}$-space. Secondly, our choice of representation, enabled us to include exactly, the surface renormalization of the J^{eff}. These were also neglected in CIBM.

The general Dyson equation for spin-wave Green's functions obtained by Al-Asadi (1980) was adopted in deriving the enhanced surface susceptibility, where the surface perturbation matrix W^{itin} is truncated to a manageable size. It was shown that W^{itin} was the difference between the unenhanced surface and the bulk susceptibility. Using the results of section 2.5, we made the observation that the surface perturbation could be regarded as a renormalization of the bulk effective exchange integrals. The surface effective exchange integrals were computed using the results of Mathon (1983) and thus χ^o was determined by the one-electron surface propagators, moving in a spin-dependent HF potential. The mapping of the surface Itinerant problem onto the surface Heisenberg one was proved in the limit $\Delta >> E_F$. In this limit, it was shown that the matrix elements of the surface perturbation of a metallic ferromagnet followed the same format as that of a non-metallic one.

In section 3.4, based on the results of section 3.3, it was shown that the value of the normalized surface effective exchange integral $\epsilon_\perp$ deduced from W^{itin} was quite close to the true itinerant $\epsilon_{\perp}$ which is the ratio of the surface effective exchange integral $J_{\perp}^{eff}$ and its bulk value.

In section 4.1, the general formulation of Wolfram (1969) for a bulk impurity in a metal, was extended to magnetic impurities in and above the surface of metallic ferromagnets. Each has been looked at in detail in sections 4.2 and 4.3.

In section 4.2, the work involved in computing the surface impurity effective exchange integral was shown. The same approach as in Chapter 3 was adopted. The general theory was applied to a Ni surface and the surface effective exchange integrals of a Ni surface were computed (Fig 1 (a)). Also, an impurity atom was then buried in that surface and surface impurity effective exchange integrals were computed. (Fig 2 (a)).

In section 4.3, an impurity situated above a metallic substrate was discussed. One of the main ingredients of the problem is that the presence of such an atom influences the surface charge density strongly (at least) in its immediate vicinity. This problem was overcome by introducing an adjustable potential for the surface atom. This was interpreted as having an impurity atom in the surface plane, which lead to a self-consistent HF problem which was then solved. Surfaces of Ni and Pd were considered and modelled by a single degenerate band. The adatom effective exchange integrals were then computed for the parameters appropriate to Ni and Pd. These are shown in Figs 2(a) and (b). It is easy to see that with increasing attractive potential on the adatom, the integrals decrease (in both cases). Such behaviour suggested that they might become zero for some critical value of adatom potential. This would imply loss of stability of the ferromagnetic ground-state of the adatom.

In section 4.4, this problem was investigated further. A strong ferromagnet was considered where there exists no ↓-spin extended states in the band. We then found the range of adatom HF potential V_1 and hopping integral T, where the ↓-spin bound-state could occur. However, in doing so, we discovered an ↑-spin bound-state below the band. Fig 3 shows the range of V_1,T for which such a bound-state occurs. The occupation number and energy level at which an ↑-spin bound state occurred were computed by deriving the appropriate adatom Green's function.

In section 4.5, the application of the general theory for surface impurity described in Sec 4.4, to Fe impurity on a Pd substrate (which was investigated by Bergmann (1980)), was discussed. Using the appropriate values of parameters for Fe on Pd, we found that ↓-spin bound-state does occur. This means that for such a system, the ferromagnetic coupling becomes unstable. This is our explanation for the absence of moment he had observed.

APPENDIX A;

Derivation of D

For a cubic crystal ; the excitation energy is $\hbar\omega \simeq Dq^2$, where q is the magnitude of the wave-vector and D, we are about to derive.

We start with the 'secular equation' :

$$I_{\text{eff}}^{-1} = \frac{1}{N} \sum_{\underline{k}}^{*} \frac{1}{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \Delta - \hbar\omega} \tag{A1}$$

where $\sum\limits_{\underline{k}}^{*}$ denotes a sum over $\underline{k}$ shuch that

$$\epsilon_{\underline{k}} < \epsilon_F^{\uparrow}$$

$$\epsilon_{\underline{k}+\underline{q}} > \epsilon_F^{\downarrow}$$

$$\text{ie } \sum_{\underline{k}}^{*} \rightarrow \sum_{\underline{k}} n_{\underline{k}\uparrow} - n_{\underline{k}+\underline{q}\downarrow}$$

and

$$\Delta = \frac{1}{N} I_{\text{eff}} (n_{\uparrow} - n_{\downarrow}) \tag{A2}$$

is the change in magnetic energy ; I is the interaction energy of two electrons of opposite spin sitting on the same atomic site.

Thus,

$$\sum_{\underline{k}}^{*} \frac{1}{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \Delta - \hbar\omega} = \sum_{\underline{k}} \frac{n_{\underline{k}\uparrow} - n_{\underline{k}+\underline{q}\downarrow}}{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \Delta - \hbar\omega} \qquad (A3)$$

$$= \sum_{\underline{k}} \frac{n_{\underline{k}\uparrow}}{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \Delta - \hbar\omega} - \sum_{\underline{k}} \frac{n_{\underline{k}+\underline{q}\downarrow}}{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \Delta - \hbar\omega} \qquad (A4)$$

Let $\underline{k} + \underline{q} \rightarrow \underline{k}'$

Therefore,

$$\sum_{\underline{k}} \frac{n_{\underline{k}+\underline{q}\downarrow}}{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \Delta - \hbar\omega} \rightarrow \sum_{\underline{k}'} \frac{n_{\underline{k}'\downarrow}}{\epsilon_{\underline{k}'} - \epsilon_{\underline{k}'-\underline{q}} + \Delta - \hbar\omega}$$

$$= \sum_{\underline{k}'} \frac{n_{\underline{k}'\downarrow}}{\epsilon_{\underline{k}'} - \epsilon_{\underline{k}'+\underline{q}} + \Delta - \hbar\omega}$$

(for $\epsilon_{\underline{k}'-\underline{q}} = \epsilon_{-(\underline{k}'-\underline{q})}$ and $\epsilon_{\underline{k}'} = \epsilon_{-\underline{k}'}$)

$$= \sum_{\underline{k}} \frac{n_{\underline{k}\downarrow}}{\epsilon_{\underline{k}} - \epsilon_{\underline{k}+\underline{q}} + \Delta - \hbar\omega} \qquad (A5)$$

Using Eqs (A4) and (A5) in Eq (A1), we have

$$I_{\text{eff}}^{-1} = \frac{1}{N}\sum_{\underline{k}} \frac{n_{\underline{k}\uparrow}}{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \Delta - \hbar\omega} - \frac{1}{N}\sum_{\underline{k}} \frac{n_{\underline{k}\downarrow}}{\epsilon_{\underline{k}} - \epsilon_{\underline{k}+\underline{q}} + \Delta - \hbar\omega} \quad (A6)$$

Now consider $\dfrac{1}{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \Delta - \hbar\omega}$.

For a given small $\underline{q}$ (→ small ω) , the above expression can be expanded in powers of $\frac{1}{\Delta}$.

i.e.

$$(\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \Delta - \hbar\omega)^{-1} = \Delta^{-1}\left[1 + \frac{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} - \hbar\omega}{\Delta}\right]^{-1}$$

$$= \Delta^{-1}\left[1 - \frac{(\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} - \hbar\omega)}{\Delta} + \frac{(\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} - \hbar\omega)^2}{\Delta^2} - \ldots\right]$$

$$= \frac{1}{\Delta} - \frac{(\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} - \hbar\omega)}{\Delta^2} + \frac{(\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} - \hbar\omega)^2}{\Delta^3} - \ldots \quad (A7)$$

Similarly,

$$(\epsilon_{\underline{k}} - \epsilon_{\underline{k}+\underline{q}} + \Delta - \hbar\omega)^{-1}$$

$$= \frac{1}{\Delta} + \frac{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \hbar\omega}{\Delta^2} + \frac{(\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \hbar\omega)^2}{\Delta^3} + \ldots \quad (A8)$$

We shall neglect the terms of $O(\frac{1}{\Delta})^4$.

Using Eq (A7), we can write

$$\sum_{\underline{k}} \frac{n_{\underline{k}\uparrow}}{\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}} + \Delta - \hbar\omega} = \frac{1}{\Delta}\sum_{\underline{k}} n_{\underline{k}\uparrow}$$

$$- \frac{1}{\Delta^2}\sum_{\underline{k}} n_{\underline{k}\uparrow}(\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}}) + \frac{1}{\Delta^2}\hbar\omega \sum_{\underline{k}} n_{\underline{k}\uparrow}$$

$$+ \frac{1}{\Delta^3}\sum_{\underline{k}} n_{\underline{k}\uparrow}(\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}})^2$$

$$+ \frac{1}{\Delta^3} 2\hbar\omega \sum_{\underline{k}} n_{\underline{k}\uparrow}(\epsilon_{\underline{k}+\underline{q}} - \epsilon_{\underline{k}})$$

$$+ \frac{1}{\Delta^3} \cancelto{0}{\hbar^2\omega^2} \sum_{\underline{k}} n_{\underline{k}\uparrow}$$

(since ω is small)

$$= \frac{1}{\Delta} n_\uparrow - \frac{1}{\Delta^2}\frac{1}{6} q^2 \sum_{\underline{k}} n_{\underline{k}\uparrow} \nabla^2 \epsilon_{\underline{k}} + \frac{1}{\Delta^2} Dq^2 n_\uparrow$$

$$+ \frac{1}{\Delta^3}\frac{1}{3} q^2 \sum_{\underline{k}} n_{\underline{k}\uparrow} (\nabla\epsilon_{\underline{k}})^2 - \frac{1}{\Delta^3} 2 Dq^2 \cancelto{0}{\frac{1}{3} q^2} \sum_{\underline{k}\uparrow} n_{\underline{k}\uparrow} \nabla^2 \epsilon_{\underline{k}}$$

(since q is small)

$$= \frac{1}{\Delta^2} Dq^2 n_\uparrow + \frac{1}{\Delta} n_\uparrow - \frac{1}{6\Delta^2} q^2 \sum_{\underline{k}} n_{\underline{k}\uparrow} \nabla^2 \epsilon_{\underline{k}}$$

$$+ \frac{1}{3\Delta^3} q^2 \sum_{\underline{k}} n_{\underline{k}\uparrow} (\nabla\epsilon_{\underline{k}})^2 \quad . \qquad \text{(A9)}$$

And similarly,

$$\sum_{\underline{k}} \frac{n_{\underline{k}\downarrow}}{\epsilon_{\underline{k}} - \epsilon_{\underline{k}+\underline{q}} + \Delta - \hbar\omega} = \frac{1}{\Delta^2} Dq^2 n_\downarrow + \frac{1}{\Delta} n_\downarrow$$

$$+ \frac{1}{6\Delta^2} q^2 \sum_{\underline{k}} n_{\underline{k}\downarrow} \nabla^2 \epsilon_{\underline{k}}$$

$$+ \frac{1}{3\Delta^3} q^2 \sum_{\underline{k}} n_{\underline{k}\downarrow} (\nabla \epsilon_{\underline{k}})^2 . \qquad \text{(A10)}$$

Substituting Eqs (A9) and (A10) into Eq (A6), we get

$$N I_{\text{eff}}^{-1} = \frac{1}{\Delta^2} Dq^2 (n_\uparrow - n_\downarrow) + \frac{1}{\Delta} (n_\uparrow - n_\downarrow)$$

$$- \frac{1}{6\Delta^2} q^2 \sum_{\underline{k}} (n_{\underline{k}\uparrow} + n_{\underline{k}\downarrow}) \nabla^2 \epsilon_{\underline{k}}$$

$$+ \frac{1}{3\Delta^3} q^2 \sum_{\underline{k}} (n_{\underline{k}\uparrow} - n_{\underline{k}\downarrow}) (\nabla \epsilon_{\underline{k}})^2 . \qquad \text{(A11)}$$

Rewritting Eq (A11), we have

$$N I_{\text{eff}}^{-1} Dq^2 = (n_\uparrow - n_\downarrow) - (n_\uparrow - n_\downarrow)$$

$$+ \frac{1}{6\Delta} q^2 \sum_{\underline{k}} [(n_{\underline{k}\uparrow} - n_{\underline{k}\downarrow}) \nabla^2 \epsilon_{\underline{k}} - \frac{(n_{\underline{k}\uparrow} - n_{\underline{k}\downarrow})}{\Delta} (\nabla \epsilon_{\underline{k}})^2]$$

(A12)

Thus,

$$D = \frac{1}{3(n_\uparrow - n_\downarrow)} \sum_{\underline{k}} [\frac{(n_{\underline{k}\uparrow} + n_{\underline{k}\downarrow})}{2} \nabla^2 \epsilon_{\underline{k}} - \frac{(n_{\underline{k}\uparrow} - n_{\underline{k}\downarrow})}{\Delta} (\nabla \epsilon_{\underline{k}})^2]$$

(A13)

APPENDIX B:

Green's Function of the Infinite Crystal

The Green's function of the ↑-spin particles for the infinite crystal, in the bloch-representation, is given by

$$G^{\uparrow}(\underline{k}) = \frac{1}{E - E_{\underline{k}}} \qquad (B1)$$

where

$$E_{\underline{k}} = -T \sum_{\underline{R}} e^{i\underline{k}.\underline{R}} \qquad (B2)$$

Thus, Eq (B1) can be written as

$$G^{\uparrow}_{ij}(\underline{R}) = \frac{1}{N} \sum_{\underline{k}} \frac{e^{i\underline{k}.\underline{R}}}{E - E_{\underline{k}}} \qquad (B3)$$

in the Wannier representation.

Using the translational symmetry of the infinite crystal, Eq (B3) can be written in the form

$$G^{\uparrow}_{ij}(\underline{R}) = \frac{1}{TZ} \frac{1}{N} \sum_{\underline{k}} \frac{T \sum_{\underline{R}} e^{i\underline{k}.\underline{R}}}{E - E_{\underline{k}}} \qquad (B4)$$

Substituting Eq (B2) into Eq (B4), we have

$$G^{\dagger}_{ij}(\underline{R}) = \frac{1}{TZ}\frac{1}{N}\sum_{\underline{k}} \frac{T\sum_{\underline{R}} e^{i\underline{k}\cdot\underline{R}}}{E + T\sum_{\underline{R}} e^{i\underline{k}\cdot\underline{R}}} \tag{B5}$$

which is equivalent to

$$= \frac{1}{TZ}\frac{1}{N}\sum_{\underline{k}} \frac{E + T\sum_{\underline{R}} e^{i\underline{k}\cdot\underline{R}} - E}{E + T\sum_{\underline{R}} e^{i\underline{k}\cdot\underline{R}}} \tag{B6}$$

Eq (B6) can now be simplified into

$$G^{\dagger}_{ij}(\underline{R}) = \frac{1}{TZ} - \frac{E}{TZ}\sum_{\underline{k}} \frac{1}{E - E_{\underline{k}}} \tag{B7}$$

$$= \frac{1}{TZ} - \frac{E}{TZ} G^{\dagger}_{ij}(\underline{R} = \underline{0}) \tag{B8}$$

It is easy to see that

$$\mathrm{Im}\, G^{\dagger}_{ij}(\underline{R}) = -\frac{E}{TZ}\,\mathrm{Im}\, G^{\dagger}_{ij}(\underline{R} = \underline{0}). \tag{B9}$$

APPENDIX C:

Unperturbed Bulk Ferromagnet

Consider an unenhanced (non-interacting particles) bulk (unperturbed and infinite) ferromagnet. We define the standard susceptibility of such a ferromagnet by

$$\Gamma(\underline{q},\omega) = \frac{1}{N}\sum_{\underline{k}} \frac{f_{\underline{k}\uparrow} - f_{\underline{k}+\underline{q}\downarrow}}{E_{\underline{k}+q\downarrow} - E_{\underline{k}\uparrow} - \omega} \tag{C1}$$

($\hbar = 1$)

where $f_{\underline{k}\sigma}$ is the Fermi-function given by Eq (1.2.14) ; $E_{\underline{k}\sigma}$ is the energy in σ-spin band and both $f_{\underline{k}\sigma}$ and $E_{\underline{k}\sigma}$ are such that

$$f_{\underline{k}\sigma} = \begin{cases} 1 & \text{for } E_{\underline{k}\sigma} < E_F \\ 0 & \text{for } E_{\underline{k}\sigma} > E_F \end{cases}$$

The sum over $\underline{k}$ and $\underline{q}$ are over the first Brillouin zone.

The matrix $\Gamma(\underline{q},\omega)$ in the Wannier-representation is defined by

$$\Gamma_{ij}(\omega) = \frac{1}{N}\sum_{\underline{q}} e^{iq.(\underline{R}_i - \underline{R}_j)}\,\Gamma(\underline{q},\omega) \tag{C2}$$

which is diagonal in the Bloch-representation, ie

$$\Gamma_{qq'}(\omega) = \frac{1}{N} \sum_{\underline{R}_i} \sum_{\underline{R}_j} e^{-i\underline{q}.\underline{R}_i} \Gamma_{ij}(\omega) e^{i\underline{q}.\underline{R}_j}$$

$$= \delta_{qq'} \Gamma(\underline{q},\omega) \qquad (C3)$$

Consider now an enhanced (interacting particles) bulk ferromagnet.

We define the susceptibility of such a ferromagnet in terms of the unenhanced susceptibility Γ.

Thus,

$$\chi = \Gamma + U \qquad (C4)$$

where U is the intra-atomic exchange integral between the electrons.

Using Eq (C4), we can write the Dyson equation

$$\chi = \Gamma + \Gamma U \chi \qquad (C5)$$

Therefore, in the operator form, we have

$$\chi = \frac{\Gamma}{I - U\Gamma} \qquad (C6)$$

The matrix-element of χ in the Wannier-representation is given by

$$\chi_{ij}(\omega) = \frac{1}{N} \sum_{\underline{q}} e^{i\underline{q}.(\underline{R}_i - \underline{R}_j)} \frac{\Gamma(\underline{q},\omega)}{I - U\,\Gamma(\underline{q},\omega)} \tag{C7}$$

which is diagonal in the Bloch-representation;

$$\chi_{qq'}(\omega) = \delta_{qq'} \frac{\Gamma(\underline{q},\omega)}{I - U\,\Gamma(\underline{q},\omega)} . \tag{C8}$$

APPENDIX D:

The Diagonal and Off-diagonal Green's Functions of a Pure Semi-infinite Ferromagnet

(I) The Diagonal Surface Green's Function:

The Green's function for the semi-infinite crystal with a HF perturbation V_o^{σ} in the surface plane can be obtained using the Dyson equation,

$$\bar{G}^{o\sigma} = G^{o\sigma} + G^{o\sigma} V_o^{\sigma} \bar{G}^{o\sigma} \tag{D1}$$

whose matrix-element is given by

$$\bar{G}^{o\sigma}_{nm} = G^{o\sigma}_{nm} + \sum_{p}\sum_{q} G^{o\sigma}_{np} V^{\sigma}_{pq} \bar{G}^{o\sigma}_{qm} \tag{D2}$$

which will reduce to

$$\bar{G}^{o\sigma}_{nm} = G^{o\sigma}_{nm} + G^{o\sigma}_{no} V^{\sigma}_{o} \bar{G}^{o\sigma}_{om} \tag{D3}$$

Since

$$V_{pq} = \begin{cases} V_o & \text{for } p = q = 0 \text{ ie in the surface} \\ 0 & \text{otherwise.} \end{cases}$$

Putting $n = 0$ in Eq (D3), we have

$$\bar{G}^{o\sigma}_{om} = G^{o\sigma}_{om} + G^{o\sigma}_{oo} V^{\sigma}_{o} \bar{G}^{o\sigma}_{om} \qquad \text{(D4)}$$

which gives

$$\bar{G}^{o\sigma}_{om} = \frac{G^{o\sigma}_{om}}{1 - G^{o\sigma}_{oo} V^{\sigma}_{o}} \qquad \text{(D5)}$$

Substituting Eq (D5) into Eq (D3), we have

$$\bar{G}^{o\sigma}_{nm} = G^{o\sigma}_{nm} + \frac{G^{o\sigma}_{no} V^{\sigma}_{o} G^{o\sigma}_{om}}{1 - G^{o\sigma}_{oo} V^{\sigma}_{o}} \ . \qquad \text{(D6)}$$

This is the general matrix-element of a semi-infinite Green's function, where

$$G^{o\sigma}_{nm} = G^{b\sigma}(|n - m|) - G^{b\sigma}(n + m) \qquad \text{(D7)}$$

and

$$V^{\sigma}_{o} = V_{o} + I^{eff}(n^{o\bar{\sigma}} - n^{b\bar{\sigma}}) \qquad \text{(D8)}$$

If we let $\underline{R}_{||}$ be the position-vector of surface atoms, then for the atom at the origin, ie $\underline{R}_{||} = (0,0)$, we have from Eq (D6)

$$\bar{G}^{o\sigma}_{oo} = \frac{G^{o\sigma}_{oo}}{1 - G^{o\sigma} U^{\sigma}_{o}} \quad . \tag{D9}$$

where $G^{o\sigma}_{oo}$ is approximated further by

$$G^{o\sigma}_{oo} \simeq G^{b\sigma}(0) \tag{D10}$$

neglecting the second nearest-neighbour matrix-element $G^{b\sigma}(2)$.

To be consistent with the notation used in the earlier part of the work, we have chosen to use $n = m = 0$. However, for the Eq (D7) to be valid, one must use $n = m = 1$.

$G^{b\sigma}(0)$ in the Wannier representation is given by

$$G^{b\sigma}(0) \quad \frac{1}{N_{||}} \sum_{\underline{k}_{||}} G^{b\sigma}_{\underline{k}_{||}}(0) \tag{D11}$$

where

$$G^{b\sigma}_{\underline{k}_{||}}(0) = \frac{1}{N_{\perp}} \sum_{\underline{k}_{\perp}} \frac{1}{E^{\sigma} - E_{\underline{k}} + i\,\delta} \tag{D12}$$

is the same function in the mixed Bloch-Wannier representation, and

$$E_{\underline{k}} = 2T(\cos k_x a + \cos k_y a + \cos k_{\perp} a) \qquad (D13)$$

Changing the summation over $\underline{k}_{\perp}$ into an integral over the first Brillouin Zone according to

$$\sum_{k_{\perp}} \rightarrow \frac{N_{\perp} a}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} dk_{\perp} \qquad (D14)$$

We find that Eq (D12) becomes

$$G^{b\sigma}_{\underline{k}_{||}}(0) = \frac{a}{2\pi} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} \frac{1}{E - W_{\underline{k}_{||}} - 2T \cos k_{\perp} a + i\delta} \qquad (D15)$$

where

$$W_{\underline{k}_{||}} = 2T(\cos k_x a + \cos k_y a) \qquad (D16)$$

It is then easily shown that in the limit $\delta \rightarrow 0$

$$G^{b\sigma}_{\underline{k}_{||}}(0) = -i\,\mu^{-1} \qquad (D17)$$

where

$$\mu = \begin{cases} (4T^2 - \omega^2)^{\frac{1}{2}} & \text{for energies inside the band.} \\ i\,\mathrm{sign}(\omega)\,(\omega^2 - 4T^2)^{\frac{1}{2}} & \text{for energies outside the band.} \end{cases} \qquad (D18)$$

with

$$\omega = E - W_{\underline{k}_{||}} \qquad \text{(D19)}$$

For a detailed derivation of $G^{b\sigma}_{\underline{k}_{||}}$ see M D Al-Asadi ; 1980.

(II) The Off-diagonal Surface Green's Function:

Consider the surface atom at the origin whose Green's function was derived in Sec (I) and its next nearest neighbouring atom also in the surface plane. The position vector of the latter is then given by

$$\underline{R}_{||} = (o\ a) \qquad \text{(D20)}$$

We refer to the Green's function of this atom as the off-diagonal surface Green's function and denote it by $\bar{G}^{o\sigma}_{o1}$.

Putting n = 0 and m = 1 in Eq (D6), we find an expresssion for $\bar{G}^{o\sigma}_{o1}$.

$$\bar{G}^{o\sigma}_{o1} = \frac{G^{o\sigma}_{o1}}{1 - G^{o\sigma}_{oo} V^{\sigma}_{o}} \qquad \text{(D21)}$$

where $G^{o\sigma}_{oo}$ is given by Eq (D10) and $G^{o\sigma}_{o1}$ in the Wannier representation can be written as

$$G^{o\sigma}_{o1} \left(= G^{o\sigma}_{oo}(\underline{R}_{||})\right) = \frac{1}{N_{||}} \sum_{\underline{k}_{||}} G^{o\sigma}_{oo}(\underline{k}_{||})\, e^{i\underline{k}_{||}\cdot\underline{R}_{||}} \qquad \text{(D22)}$$

$$= \frac{1}{N_{||}} \sum_{\underline{k}_{||}} G^{o\sigma}_{oo}(\underline{k}_{||})\, e^{ik_y a}$$

$$= \frac{1}{N_{||}} \sum_{\underline{k}_{||}} G^{o\sigma}_{oo}(\underline{k}_{||}) \cos k_y a \qquad \text{(D23)}$$

(Since $G^{o\sigma}_{oo}(\underline{k}_{||})$ is an even function).

By symmetry, we have $\cos k_x a = \cos k_y a$, so that

$$\cos k_y a = \tfrac{1}{2}(\cos k_x a + \cos k_y a) \qquad \text{(D24)}$$

Putting $X = k_x a$, $Y = k_y a$ and using Eq (D24) in Eq (D23), we obtain

$$G^{0\sigma}_{01} = \tfrac{1}{2} \frac{1}{N_{||}} \sum_{\underline{k}_{||}} G^{0\sigma}_{00}(\underline{k}_{||})(\cos X + \cos Y). \qquad \text{(D25)}$$

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