

## CHAPTER IV



### THEORY OF LOCALIZED STATE IN METALS.

The primary purpose of this chapter is to review briefly the theory of localized state in metals, and to discuss some points of special interest in detail. The theory is developed with the aim of attacking the general problems of magnetism in metals. An attempt is made to understand the magnetic properties of a single transition-element impurity in a metallic environment. For an isolated atom, it is the Coulomb repulsion that makes the moment aligned parallel in accordance with Hund's rule. There is no doubt that the same interaction also plays a dominant role in the formation of the moment in metals. It should be noted, however, that the atomic orbitals are no longer the exact eigen-states of the one-electron problem in metals and that there exists a tendency to delocalize the electron from the atomic orbital. This tendency acts against the formation of the moment. The Hume-Rothery rules suggest that the impurity atom will lose some of its valence electrons to the conduction band of metals and leave an ion core with excess charge  $+Ze$  (relative to the host metal's ion core charge). Thus, the density of conduction electrons around the impurity ion core is relatively high, in order that the charge  $+Ze$  be neutralized. Similarly for negative excess charge  $-Ze$ , it should be observed

that around the impurity ion core there will be a concentration of positive charge (or hole). The problem is to understand the behavior of the electron gas scattering by the spherical potential field arising from the impurity ion core.

#### 4.1 The behavior of an electron in spherical potential field.<sup>76-78</sup>

Let an electron be enclosed in a sphere of large radius  $R$  and move in a spherical symmetric field of potential  $V(r)$ . This  $V(r)$  is usually taken to be a screened Coulomb potential. The Schrödinger equation for free electron is

$$(\nabla^2 + k^2) \cdot \psi_0(\vec{r}) = 0 , \quad (4.1.1)$$

while the equation for electron in potential field  $V(r)$  is

$$(\nabla^2 + k^2 - U(r)) \cdot \psi(\vec{r}) = 0 \quad (4.1.2)$$

In these two equations, we define

$$k^2 = 2mE/\hbar^2$$

$$\text{and} \quad U(r) = 2mV(r)/\hbar^2 .$$

For spherical symmetric space, the wave function  $\psi_0(\vec{r})$  and  $\psi(\vec{r})$  can be separated into radial and spherical harmonics functions. Since the spherical harmonics solution for the two cases are the identical, our interest center on the radial part of the two equations. The corresponding radial part of 4.1.1 and 4.1.2 are

$$\left[ \frac{1}{r^2} \cdot \frac{d}{dr} \left( r^2 \cdot \frac{d}{dr} \right) + k^2 - \frac{\ell(\ell+1)}{r^2} \right] \cdot R_0(r) = 0 \quad (4.1.3)$$

$$\text{and} \quad \left[ \frac{1}{r^2} \cdot \frac{d}{dr} \left( r^2 \cdot \frac{d}{dr} \right) + k^2 - \frac{\ell(\ell+1)}{r^2} - U(r) \right] \cdot R_0(r) = 0 \quad (4.1.4)$$

These two equations can be simplified by defining

$$P_0(r) = R_0(r)/r \quad (4.1.5.a)$$

$$\text{and} \quad P(r) = R(r)/r. \quad (4.1.5.b)$$

Introducing a parameter  $\epsilon$ , the two equations become

$$\left[ P''(r) + k^2 - \frac{\ell(\ell+1)}{r^2} - \epsilon U(r) \right] \cdot P(r) = 0. \quad (4.1.6)$$

This equation reduces to the case of electron in free space when  $\epsilon=0$  and to the case of electron in the potential  $V(r)$  when  $\epsilon=1$ .

The asymptotic solution for large  $r$  of 4.1.6 is

$$P(r) = C \cdot \sin(kr - \frac{1}{2}\ell\pi + \eta_\ell(k)) \quad (4.1.7)$$

$$\text{or} \quad R(r) = C/r \cdot \sin(kr - \frac{1}{2}\ell\pi + \eta_\ell(k)). \quad (4.1.8)$$

This asymptotic expression has been discussed by Mott and Massey (1949)<sup>79</sup>. They showed that the solution exist only if  $V(r)$  tend to zero faster than  $1/r$ .  $\eta_\ell(k)$  is called phase shift and depend directly to  $\ell$  and  $k$ . For  $\epsilon=0$ ,  $\eta_\ell(k)$  is zero, while for  $\epsilon=1$ ,  $\eta_\ell(k)$  can only be find by numerical calculation. The boundary condition is that the wave function vanishes at  $r=R$ . Thus the allowed value of  $k$  satisfies

$$kR - \frac{1}{2}\ell\pi + \eta_{\ell}(k) = n\pi ; n = 0, 1, 2, 3 \dots \quad (4.1.9)$$

C is the normalization required for radial wave function to satisfy the condition

$$\int_0^R dr \cdot 4\pi r^2 \cdot P^2(r) = 4\pi \int_0^R dr \cdot P^2(r) = 1. \quad (4.1.10)$$

We now define  $\bar{P}(r)$  to be the function corresponding to  $\bar{k} = k + dk$ , and so we have

$$\left[ \bar{P}''(r) + \bar{k}^2 - \frac{\ell(\ell+1)}{r^2} - \epsilon U(r) \right] \cdot \bar{P}(r) = 0. \quad (4.1.11)$$

Multiplying 4.1.6 by  $\bar{P}(r)$  and 4.1.11 by  $P(r)$ , and then subtracting the two, as well as integrating from 0 to any  $r$ , we get

$$\int_0^r dr \cdot (\bar{P}P'' - P\bar{P}'') + (k^2 - \bar{k}^2) \cdot \int_0^r dr \cdot P\bar{P} = 0,$$

which is equivalent to

$$\int_0^r dr \cdot \frac{d}{dr} (\bar{P}P' - P\bar{P}') + (k^2 - \bar{k}^2) \cdot \int_0^r dr \cdot P\bar{P} = 0.$$

or

$$\left[ \bar{P}P' - P\bar{P}' \right]_0^r + (k^2 - \bar{k}^2) \cdot \int_0^r dr \cdot P\bar{P} = 0. \quad (4.1.12)$$

Since  $\bar{k} = k + dk$ , we can write

$$\bar{P} = P + \frac{\partial P}{\partial k} \cdot dk$$

and  $P(0) = 0$ . Then 4.1.12 becomes

$$\frac{\partial P}{\partial k} \cdot \frac{\partial P}{\partial r} - P \cdot \frac{\partial^2 P}{\partial k \partial r} = 2k \cdot \int_0^r dr \cdot P^2. \quad (4.1.13)$$

For large  $r$  we can apply 4.1.7 and the normalization condition 4.1.10 to 4.1.13 to get

$$C^2 \cdot \left[ \left( r + \frac{\partial \eta}{\partial k} \right) \cdot k - \frac{1}{2} \sin 2(kr - \frac{1}{2} \ell \pi + \eta_\ell) \right] = 2k/4\pi \cdot \int_0^r dr \cdot 4\pi P^2. \quad (4.1.14)$$

If  $r=R$ , we have

$$C = \left[ 2\pi R \cdot \left( 1 + \frac{1}{R} \cdot \frac{\partial \eta}{\partial k} \right) \right]^{-1/2} = (2\pi R)^{-1/2}. \quad (4.1.15)$$

If we now go back to equation 4.1.14 and break it into two equations corresponding to  $\ell = 1$  and  $0$ , we get

$$\int_0^r dr \cdot 4\pi \cdot (P^2 - P_0^2) = \frac{1}{R} \cdot \left[ \frac{\partial \eta}{\partial k} - \frac{\sin \eta}{k} \cdot \cos(2kr - \ell \pi + \eta_\ell) \right], \quad (4.1.16)$$

where we have subtracted the two and divide by  $k$ . This is the localization due to a single  $\ell$ -state. Since the degeneracy of  $\ell$ -state is  $2(2\ell + 1)$ , the total number of  $\ell$ -state between  $k$  and  $k+dk$  is

$$\begin{aligned} \Delta N_k &= 2 \sum_{\ell} (2\ell + 1) \cdot \int_0^r dr \cdot 4\pi (P^2 - P_0^2) \\ &= \frac{2}{R} \sum_{\ell} (2\ell + 1) \cdot \left[ \frac{\partial \eta}{\partial k} - \frac{\sin \eta}{k} \cdot \cos(2kr - \ell \pi + \eta_\ell) \right] \cdot \end{aligned}$$

From 4.1.9 the allowed number of state in  $dk$  is  $Rdk/\pi$ . Thus the total number of electron accumulated is given by

$$\Delta N = \int_0^{k_F} dk \cdot \Delta N_k \cdot R/\pi,$$

$$\text{or } \Delta N = \frac{2}{\pi} \sum_{\ell} (2\ell+1) \cdot \int_0^{k_F} dk \cdot \left[ \frac{\partial \eta_{\ell}}{\partial k} - \frac{\sin \eta_{\ell}}{k} \cdot \cos(2kr - \ell\pi + \eta_{\ell}) \right] \quad (4.1.17)$$

The second term is called oscillation term.<sup>76,77</sup> This oscillation term can be integrated by part to give

$$\begin{aligned} \text{the oscillation integral term} &= \frac{\sin \eta_{\ell}(k_F)}{k_F r} \cdot \sin(2k_F r - \ell\pi + \eta_{\ell}(k_F)) + O(1/r^2), \\ \text{Thus } \Delta N &= \frac{2}{\pi} \sum_{\ell} (2\ell+1) \cdot \left[ \eta_{\ell}(k_F) - \frac{\sin \eta_{\ell}(k_F)}{k_F r} \cdot \sin(2k_F r - \ell\pi + \eta_{\ell}(k_F)) \right]. \quad (4.1.18) \end{aligned}$$

The local density charge  $\rho(r)$  is related to  $\Delta N$  by

$$\begin{aligned} \rho(r) &= \frac{1}{4\pi r^2} \cdot \frac{\Delta N}{\partial r} \\ &= \frac{-1}{2\pi^2 r^3} \cdot \sum_{\ell} (2\ell+1) \cdot \sin \eta_{\ell}(k_F) \cdot \cos(2k_F r - \ell\pi + \eta_{\ell}(k_F)) \\ &= \frac{-1}{2\pi^2 r^3} \cdot \sum_{\ell} (2\ell+1) \cdot (-1)^{\ell} \cdot \sin \eta_{\ell}(k_F) \cdot \cos(2k_F r + \eta_{\ell}(k_F)). \end{aligned} \quad (4.1.19)$$

By discarding the oscillation term in 4.1.18, we have total number of electron needed to screen the excess charge  $\pm Ze$ . Thus

$$Z = \frac{2}{\pi} \sum_{\ell} (2\ell+1) \cdot \eta_{\ell}(k_F). \quad (4.1.20)$$

This is the famous Friedel's sum rule,<sup>78</sup> which is the important self-consistency condition required of the potential  $V(r)$ .

Let  $R_0$  be the radius where the potential  $V(r)$  vanish (Thomas-Fermi screening radius). It is a well known result of von Laue's theorem (1914) that the electronic density far away (greater than  $1/k_F$  or about lattice constant) from boundary surface is independent of boundary condition on the surface.<sup>80</sup> From 4.1.19 and von Laue's theorem it can be concluded that the valence electron of impurity atom, which are lost to the conduction band, are still localized around the impurity ion core. More details about this localization will be discussed in the next section. Note that, the localized electron around the impurity ion core are coming from conduction band.

#### 4.2 Virtual bound state.<sup>76</sup>

If the potential  $V(r)$  is strong enough to accept a certain bound state with quantum number  $\ell$ , one of valence electrons of the impurity will remain bound in the impurity site. Its energy will be below the minimum band edge of conduction band. Thus the **impurity** atom will act as if possessed of excess charge  $Z-1$  rather than  $Z$ . The  $V(r)$  must be then reformulated. This bound state may be thought of as being as subtracted from the bottom of the Fermi distribution of the conduction band. The reformulated potential  $V(r)$  will then be less attractive. Therefore the bound states increase its

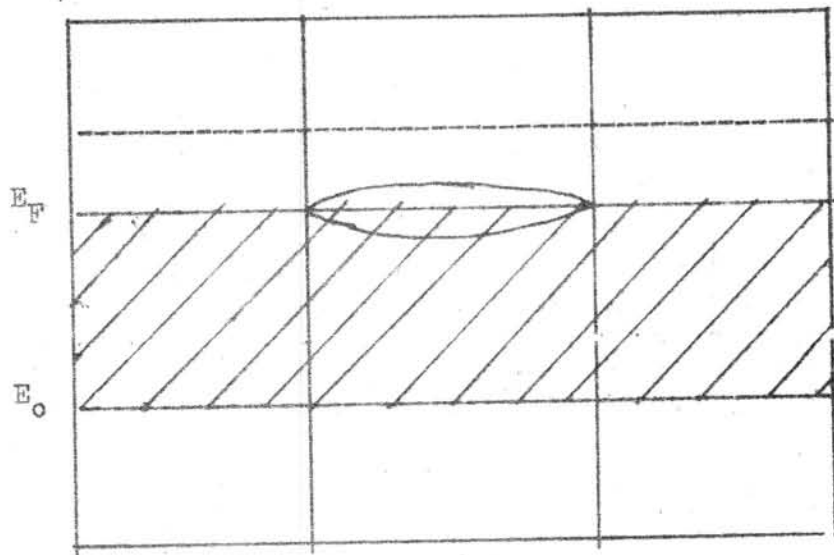


Fig.4.2.1: the diagrammatic representation of the virtual bound state.

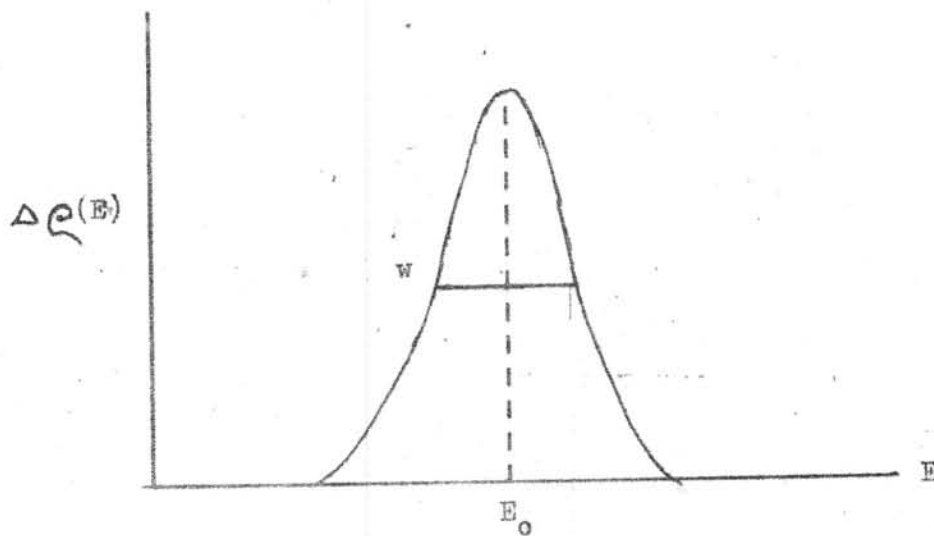


Fig.4.2.2: The density of state change.



energy and eventually merges itself into the continuum of conduction band states. It is however useful to think of the state as still existing as a virtual bound state. These states have the wave function which the distance of the atomic radius look very much like atomic wave function, but at large distance from the impurity site these functions will not decay exponentially since this type behavior corresponds to positive energy relative to minimum band edge. However, the wave function will have decayed to small value by the time it leave the impurity sites (see 4.1.19). The virtual state can be represented diagrammatically like Fig.4.2.1. The change in density of states is something like Fig 4.2.2. The width of the density of states change is related to the time that the electron take to be localized at the impurity site through the uncertainty principle

$$\tau = \hbar / w.$$

There are many details of phase shift analysis <sup>76-78,81</sup> which are beyond the scope of interest. Since we are just interested in existence of the virtual state, which behaves as an intermediate between localized and extended states, we shall not to into the phase shift analysis.

#### 4.3 The improved model of localized magnetic moment in metals.

Based on Friedel's qualitative idea of the virtual state of impurity in metals, two important papers have extended the

understanding of the problem and have provided some quantitative result.<sup>38,82</sup> These two papers are based on the same idea but different approach.

The first is Anderson's paper on the hybridization of localized state and extended states, or s-d covalent admixing.<sup>38</sup> In this model, the localized states are no longer eigen-state but have a finite width in energy, i.e. we have virtual bound state associated with the impurity atom. When the interactions between electron in impurity site are taken into account, the possibility of spin-splitting of the level and the existence of localized magnetic moment can be determined. This model is considered to be applicable to the following case:<sup>83</sup>

- i) transition impurity atoms in noble and other non-transition metals,
- ii) rare-earth impurity atoms in various metals including transition metals,
- iii) it is also possible to apply this model, with some modification in its interpretation, to transition impurity atoms in host transition metals.

This model will be shown later in section V to be applicable to chemisorption of hydrogen on metals, the subject of this thesis.

A month later Wolff proposed a model which was based on Koster and Slater's Green function method<sup>73-75</sup> to formulate the

mathematical treatment of Friedal's idea.<sup>82</sup> This model has been improved by Clogston.<sup>84-86</sup> This model can be applied to transition metals alloys to which Anderson model is not directly applicable.

#### 4.4 Anderson model.<sup>38</sup>

Beginning with the unperturbed Hamiltonian  $H_0$  is taken to be that for the isolated system,  $H_0$  is obtain by the direct combination of  $H_A^0$  and  $H_M^0$ , the Hamiltonian of free impurity atom and free host metals. The localized orbitals set  $\{|\ell\sigma\rangle\}$  and the Bloch state set  $\{|k\sigma\rangle\}$  of spin  $\sigma$  are the sets of eigen-states of the two isolated Hamiltonian  $H_A^0$  and  $H_M^0$ . As we already mentioned that the states of the system have the characteristics of both localized and extended state. The nearer the energy is to that of the atomic orbital the more localize it be. If the  $\{|\ell\sigma\rangle\}$  are all orthogonalized with  $\{|k\sigma\rangle\}$ , the set  $\{|\ell\sigma\rangle, |k\sigma\rangle\}$  form the set of eigen-state of  $H_0$ .

This eigen-state set is overcomplete since  $\{|k\sigma\rangle\}$  is complete. However, the overcompleteness can be easily taken off by proposing some overlap, which has been proved to give the result which are independent of such overlap.<sup>87</sup> Thus  $\{|\ell\sigma\rangle, |k\sigma\rangle\}$  can be used as basis one-electron vectors of the system.

The next step is to introduce one-electron coupling term  $H_{AM}$  into the Hamiltonian. It would be a great mistake if we miss the correlation term  $H_{corr}$  since the existence of localized magnetic moment is due to this term. The Hamiltonian of the system becomes

$$H = H_M^0 + H_A^0 + H_{AM} + H_{corr} \quad (4.4.1)$$

This approximate Hamiltonian is called Anderson Hamiltonian. It can be written in the second quantization formalism<sup>88</sup> as

$$\begin{aligned} H_M^0 &= \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} \quad , \\ H_A^0 &= \sum_{\sigma} \epsilon_{\ell} c_{\ell\sigma}^\dagger c_{\ell\sigma} \quad , \\ H_{AM} &= \sum_{k\sigma} (V_{k\ell} c_{k\sigma}^\dagger c_{\ell\sigma} + H.C.) \quad , \\ H_{corr} &= \frac{1}{2} U \sum_{\sigma} n_{\ell\sigma} n_{\ell\bar{\sigma}} \\ H &= \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{\sigma} \epsilon_{\ell} c_{\ell\sigma}^\dagger c_{\ell\sigma} + \sum_{k\sigma} (V_{k\ell} c_{k\sigma}^\dagger c_{\ell\sigma} + H.C.) \\ &\quad + \frac{1}{2} U \sum_{\sigma} n_{\ell\sigma} n_{\ell\bar{\sigma}} \quad (4.4.2) \end{aligned}$$

which contain all of the Friedel's idea as an underling shadow. The  $c_{k\sigma}^\dagger$  and  $c_{k\sigma}$  are defined as creation and annihilation operators for Bloch k-state with spin  $\sigma$ . The same definition are given for  $c_{\ell\sigma}^\dagger$  and  $c_{\ell\sigma}$  of localized state, also.

$$n_{k\sigma} = \sum_{k\sigma} c_{k\sigma}^\dagger c_{k\sigma}$$



The spin  $\bar{\sigma}$  denote the opposite of spin  $\sigma$ .

As with all perturbative problems, the unperturbed system is taken to be that of an well known system. Such system is described by  $H_A^0$  and  $H_M^0$ . The  $\epsilon_k$  is the energy of free-electron state of momentum  $k$ . The continuum of free-electron states has a density of states  $\rho(\omega)$ , which is usually assumed to be a constant. It has been point out by Anderson that the variation of  $\rho(\omega)$  has little effect on the results<sup>38</sup> (this will be discussed in detail for the chemisorption problem later, see also appendix F). The  $\epsilon_\ell$  is energy of localized orbital of free impurity atom, which can be determined with the high accuracy for almost all element.

The coupling term, which will perturb the system, is  $k$ - $\ell$  interaction or covalent admixing. The coupling coefficient  $V_{k\ell}$  is associated with the probability for electron to tunnel from impurity site into the continuum of metal, and vice versa. This will of cause destroy the localized magnetic moment of the impurity atom. Some time the coefficient will be treated as constant  $\bar{V}$ , the average, or root mean squar of  $V_{k\ell}$ , while other time it will be expanded in term of the Wannier function as

$$\begin{aligned} V_{k\ell} &= \frac{1}{\sqrt{N}} \int d\bar{r} \cdot \phi_\ell^*(\bar{r}) \cdot H_{HF} \cdot \sum_n \exp(i\bar{k} \cdot \bar{R}_n) \cdot a(\bar{r} - \bar{R}_n) \\ &= \frac{1}{\sqrt{N}} \sum_{R_n \neq 0} \exp(i\bar{k} \cdot \bar{R}_n) \cdot V(R_n) \end{aligned}$$

The latter expansion can be obtained directly by a Fourier expansion of the former expansion. If the perturbation is small we need only consider a few of the nearest neighbor terms.

Electron-electron interaction at impurity site can be approximated by constant  $U$ . The main contribution to this term is the Coulomb repulsion energy of opposite spin

$$U \approx \int d\bar{r}_1 d\bar{r}_2 \cdot |\phi_x(\bar{r}_1)|^2 \cdot (|\bar{r}_1 - \bar{r}_2|)^{-1} \cdot |\phi_x(\bar{r}_2)|^2 \cdot$$

The question of the same spin Coulomb interaction does not arise since it is not allowed by Pauli exclusion principle. Note that, this approximation is not correct even for the free impurity atom since there are many other terms arising from exchange and correlation effects.

#### 4.5 The Green function solution of Anderson Hamiltonian.

To solve the present problem, there are many techniques which are used. The easiest and most powerful one is the Green function techniques.<sup>88,89</sup> It is well known that every Hamiltonian operator has an associate operator called the resolvent operator

$$R(\omega) = [\omega I - H]^{-1},$$

which is well defined and unique, and which is generally called the Green operator. Anderson has used this Green operator to solve the problem, using what is known as Hartree-Fock approximation.<sup>38</sup>

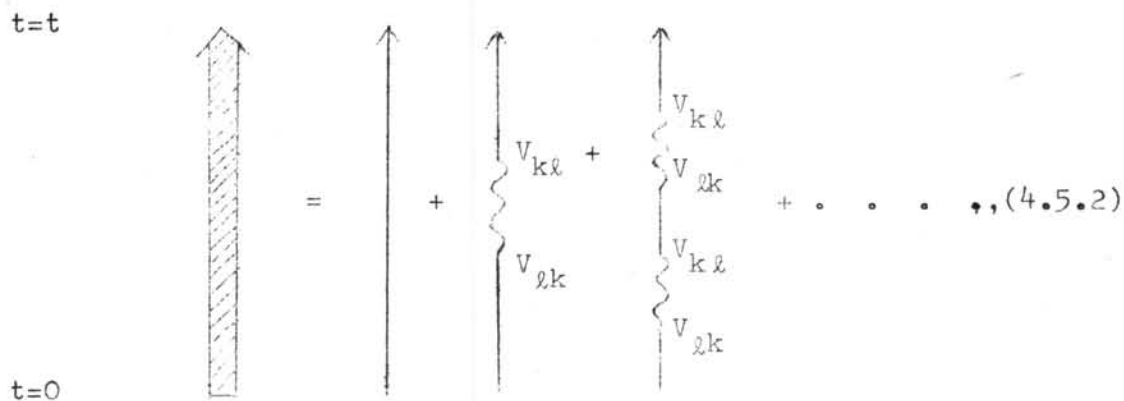
His results are limited to some range of value of the parameters (defined in previous section). In this section, we would like to work out the same problem but with a slightly different Green function, the so-called double-time Green function<sup>89</sup> (see appendix A). Hubbard (1963-4)<sup>90-92</sup> used this Green function to study the correlation effect in narrow band or transition metals. In the papers he introduced the new Hamiltonian, now call Hubbard Hamiltonian, which is the modification of Anderson Hamiltonian. The success of Hubbard arose because of a scheme being introduce. The new scheme went beyond Hartree-Fock approximation is called Hubbard decoupling scheme. The propagation of the electron in the transition metals is compared to the propagation of light in alloys. The analogy between the two is called "the alloys analoy". Hewson(1965)<sup>93</sup> used Hubbard idea to work on Anderson Hamiltonian to study the localization of magnetic moment in metals.

The retarded Green function for electron with spin  $\sigma$  at an impurity site is defined as ;<sup>89</sup>

$$G_{\ell\ell}^{\sigma}(t) = \langle\langle c_{\ell\sigma}(t), c_{\ell\sigma}^{\dagger}(0) \rangle\rangle = -i\theta(t) \cdot \langle\{c_{\ell\sigma}(t), c_{\ell\sigma}^{\dagger}(0)\}\rangle. (4.5.1)$$

Going back to 4.4.1 and 4.4.2, a little rearrangement is done in order to acheve the physical meaning of having the free impurity atom contain  $H_{\text{corr}}$ . This then leaves the covalent admixing as perturbation. The Green function defined in 4.5.1 has physical meaning of an propagator for electron being created at the impurity site at the

time 0 and propagate in a manner similar to diagram representation shown below ;



where  $\uparrow$  represent electron propagator for free impurity atom and  $\uparrow$  represent electron propagator in metals. The diagram can be solved directly by studying the analytic properties of vertex.<sup>94,95</sup> This is however very complicate task and not necessary to our study.

If the covalent admixing term is zero, the Green function will satisfy the following equation of motion ;

$$\omega G_{\ell\ell\sigma}^o(\omega) = \frac{1}{2\pi} \cdot \langle [c_{\ell\sigma}, c_{\ell\sigma}^\dagger] \rangle + \langle \langle [c_{\ell\sigma}, \bar{H}], c_{\ell\sigma}^\dagger \rangle \rangle, \quad (4.5.3)$$

where  $\bar{H}$  is the unperturbed hamiltonian

$$\bar{H} = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{\sigma} \epsilon_{\ell} c_{\ell\sigma}^\dagger c_{\ell\sigma} + \frac{1}{2} U \cdot \sum_{\sigma} n_{\ell\sigma} n_{\ell\bar{\sigma}}. \quad (4.5.4)$$

Since

$$\{c_{\ell\sigma}, c_{\ell\sigma}^\dagger\} = 1, [c_{\ell\sigma}, c_{k\sigma}^\dagger c_{k\sigma}] = 0, [c_{\ell\sigma}, c_{\ell\sigma}^\dagger c_{\ell\sigma}] = \delta_{\sigma\sigma'} c_{\ell\sigma'}$$

and  $[c_{\ell\sigma}, n_{\ell\sigma'}] = 2\delta_{\sigma\sigma'} n_{\ell\sigma'} c_{\ell\sigma'}$



the equation of motion 4.5.3 becomes

$$(\omega - \epsilon_{\lambda}) \cdot G_{\lambda\lambda\sigma}^0(\omega) = 1/2\pi + U \cdot \Gamma_{\lambda\lambda\sigma}^0(\omega), \quad (4.5.6)$$

where  $\Gamma_{\lambda\lambda\sigma}^0(\omega)$  is defined

$$\Gamma_{\lambda\lambda\sigma}^0(\omega) = \langle\langle n_{\lambda\bar{\sigma}} c_{\lambda\sigma}, c_{\lambda\sigma}^+ \rangle\rangle.$$

In turn, this Green function satisfies the equation of motion

$$\Gamma_{\lambda\lambda\sigma}^0(\omega) = \frac{1}{2\pi} \cdot \langle\{n_{\lambda\bar{\sigma}} c_{\lambda\sigma}, c_{\lambda\sigma}^+\}\rangle + \langle\langle [n_{\lambda\bar{\sigma}} c_{\lambda\sigma}, \bar{H}], c_{\lambda\sigma}^+ \rangle\rangle \quad (4.5.7)$$

We know that

$$\{n_{\lambda\bar{\sigma}} c_{\lambda\sigma}, c_{\lambda\sigma}^+\} = n_{\lambda\bar{\sigma}}, \quad [n_{\lambda\bar{\sigma}} c_{\lambda\sigma}, c_{k\sigma'}^+ c_{k\sigma'}] = 0,$$

$$[n_{\lambda\bar{\sigma}} c_{\lambda\sigma}, c_{\lambda\sigma'}^+ c_{\lambda\sigma'}] = \delta_{\sigma\sigma'} n_{\lambda\bar{\sigma}} c_{\lambda\sigma}, \quad \text{and } [n_{\lambda\bar{\sigma}} c_{\lambda\sigma}, n_{\lambda\sigma'} n_{\lambda\bar{\sigma}'}] = 2\delta_{\sigma\sigma'} n_{\lambda\bar{\sigma}}^2 c_{\lambda\sigma}. \quad (4.5.8)$$

Since  $n_{\lambda\sigma}^2 = n_{\lambda\sigma}$ , we have

$$[n_{\lambda\bar{\sigma}} c_{\lambda\sigma}, n_{\lambda\sigma'} n_{\lambda\bar{\sigma}'}] = 2\delta_{\sigma\sigma'} n_{\lambda\bar{\sigma}} c_{\lambda\sigma}.$$

Thus 4.5.7 becomes

$$\Gamma_{\lambda\lambda\sigma}^0(\omega) = \frac{\langle n_{\lambda\bar{\sigma}} \rangle}{2\pi \cdot (\omega - \epsilon_{\lambda} - U)}. \quad (4.5.9)$$

Then, we have

$$\begin{aligned}
 G_{\ell\ell\sigma}^{\circ}(\omega) &= \frac{1}{2\pi} \left[ \frac{1}{(\omega - \epsilon_{\ell})} + \frac{U \cdot \langle n_{\ell\bar{\sigma}} \rangle}{(\omega - \epsilon_{\ell}) \cdot (\omega - \epsilon_{\ell} - U)} \right] \\
 &= \frac{1}{2\pi} \left[ \frac{1 - \langle n_{\ell\bar{\sigma}} \rangle}{(\omega - \epsilon_{\ell})} + \frac{\langle n_{\ell\bar{\sigma}} \rangle}{(\omega - \epsilon_{\ell} - U)} \right] \quad (4.5.10)
 \end{aligned}$$

The result indicates that there are two type of propagators, the first has no opposite spin interaction while the second has. The probability of finding these two propagators is determined by the number of spin electron occupy in the impurity site, as show in the equation 4.5.10.

In contrast, the Hartree-Fock approximation give us the average of these two propagators. Decoupling  $\Gamma_{\ell\ell\sigma}^{\circ}(\omega)$  in 4.5.6 in the following way

$$\Gamma_{\ell\ell\sigma}^{\circ}(\omega) = \langle n_{\ell\bar{\sigma}} \rangle \cdot G_{\ell\ell\sigma}^{\circ}(\omega) ,$$

we have

$$G_{\ell\ell\sigma}^{\circ}(\omega) = \frac{1}{2\pi} \cdot (\omega - \epsilon_{\ell\sigma})^{-1} ,$$

where 
$$\epsilon_{\ell\sigma} = \epsilon_{\ell\sigma} - U \cdot \langle n_{\ell\bar{\sigma}} \rangle .$$

The next step is to perturb the system by the covalent admixing. Again, the equation of motion for  $G_{\ell\ell}^{\sigma}$ ,  $G_{\ell k}^{\sigma}$ ,  $G_{k\ell}^{\sigma}$ ,  $G_{kk}^{\sigma}$ , are

$$G_{\ell\ell}^{\sigma} = \frac{1}{2\pi} \langle \{c_{\ell\sigma}, c_{\ell\sigma}^{\dagger}\} \rangle + \langle\langle [c_{\ell\sigma}, H], c_{\ell\sigma}^{\dagger} \rangle\rangle, \quad (4.5.11.a)$$

$$G_{\ell k}^{\sigma} = \frac{1}{2\pi} \langle \{c_{\ell\sigma}, c_{k\sigma}^{\dagger}\} \rangle + \langle\langle [c_{\ell\sigma}, H], c_{k\sigma}^{\dagger} \rangle\rangle \quad (4.5.11.b)$$

$$G_{k\ell}^{\sigma} = \frac{1}{2\pi} \langle \{c_{k\sigma}, c_{\ell\sigma}^{\dagger}\} \rangle + \langle\langle [c_{k\sigma}, H], c_{\ell\sigma}^{\dagger} \rangle\rangle \quad (4.5.11.c)$$

$$G_{kk'}^{\sigma} = \frac{1}{2\pi} \langle \{c_{k\sigma}, c_{k'\sigma}^{\dagger}\} \rangle + \langle\langle [c_{k\sigma}, H], c_{k'\sigma}^{\dagger} \rangle\rangle \quad (4.5.11.d)$$

We also have

$$\{c_{i\sigma}, c_{j\sigma'}\} = \delta_{ij} \delta_{\sigma\sigma'} \quad (4.5.12)$$

and

$$\begin{aligned} [c_{j\sigma'}, H] &= \sum_{k\sigma} \epsilon_k [c_{j\sigma'}, c_{k\sigma}^{\dagger} c_{k\sigma}] + \sum_{\ell\sigma} \epsilon_{\ell} [c_{j\sigma'}, c_{\ell\sigma}^{\dagger} c_{\ell\sigma}] \\ &+ \frac{1}{2} \sum_{\ell\sigma} \epsilon_{\ell} [c_{j\sigma'}, n_{\ell\sigma}^{\dagger} n_{\ell\sigma}] + \sum_{k\sigma} \left\{ V_{k\ell} [c_{j\sigma'}, c_{k\sigma}^{\dagger} c_{\ell\sigma}] + V_{\ell k} [c_{j\sigma'}, c_{\ell\sigma}^{\dagger} c_{k\sigma}] \right\}, \end{aligned} \quad (4.5.13)$$

where

$$\begin{aligned} [c_{j\sigma'}, c_{k\sigma}^{\dagger} c_{k\sigma}] &= \delta_{jk} \delta_{\sigma\sigma'} c_{k\sigma}, \quad [c_{j\sigma'}, c_{\ell\sigma}^{\dagger} c_{\ell\sigma}] = \delta_{j\ell} \delta_{\sigma\sigma'} c_{\ell\sigma}, \\ [c_{j\sigma'}, n_{\ell\sigma}^{\dagger} n_{\ell\sigma}] &= \delta_{j\ell} \delta_{\sigma\sigma'} n_{\ell\sigma}^{\dagger} c_{\ell\sigma}, \quad [c_{j\sigma'}, c_{k\sigma}^{\dagger} c_{\ell\sigma}] = \delta_{jk} \delta_{\sigma\sigma'} c_{\ell\sigma}, \quad (4.5.14) \\ [c_{j\sigma'}, c_{\ell\sigma}^{\dagger} c_{k\sigma}] &= \delta_{j\ell} \delta_{\sigma\sigma'} c_{k\sigma}. \end{aligned}$$

Applying 4.5.14 to 4.5.13 and putting it back to 4.5.11.a, b, c, d as  $j=l$  or  $k$  in the equation, we get

$$(\omega - \epsilon_l) \cdot G_{ll}^\sigma = 1/2\pi + U \cdot \Gamma_{ll\sigma}^{ll} + \sum_k V_{lk} G_{kl}^\sigma, \quad (4.5.15.a)$$

$$(\omega - \epsilon_l) \cdot G_{lk}^\sigma = U \cdot \Gamma_{lk\sigma}^{ll} + \sum_{k'} V_{lk'} G_{k'k}^\sigma, \quad (4.5.15.b)$$

$$(\omega - \epsilon_k) \cdot G_k^\sigma = V_{kl} G_{ll}^\sigma, \quad (4.5.15.c)$$

$$(\omega - \epsilon_k) \cdot G_{kk'}^\sigma = \delta_{kk'} / 2\pi + V_{kl} G_{lk'}^\sigma \quad (4.5.15.d)$$

Substituting  $G_{kl}^\sigma$ ,  $G_{kk'}^\sigma$  in 4.5.15.a, b by the expression 4.5.15.c,d, we get

$$(\omega - \epsilon_l - \Sigma_o) \cdot G_{ll}^\sigma = 1/2\pi + U \cdot \Gamma_{ll\sigma}^{ll} \quad (4.5.16.a)$$

$$\text{and} \quad (\omega - \epsilon_l - \Sigma_o) \cdot G_{lk}^\sigma = U \cdot \Gamma_{lk\sigma}^{ll} + V_{lk} / (2\pi \cdot (\omega - \epsilon_k)), \quad (4.5.16.b)$$

$$\text{where} \quad \Sigma_o = \sum_k |V_{kl}|^2 / (\omega - \epsilon_k + i\delta) \quad (4.5.17)$$

and where the two-particle Green function is defined on

$$\Gamma_{kl\sigma}^{ij} = \langle \langle c_{i\bar{\sigma}}^\dagger c_{j\bar{\sigma}} c_{k\sigma}, c_{l\sigma}^\dagger \rangle \rangle \quad (4.5.18)$$

The self-energy  $\Sigma_o$  arise from electron interacting with itself through the covalent admixing process. Equation 4.5.16.a, b show the two-particle Green function is dependent on the single-particle Green function.

Both  $\Gamma_{\ell\ell\sigma}^{\ell\ell}$  and  $\Gamma_{\ell k\sigma}^{\ell\ell}$  satisfy the equation of motion

$$\Gamma_{\ell\ell\sigma}^{\ell\ell} = \frac{1}{2\pi} \langle \{n_{\ell\bar{\sigma}} c_{\ell\sigma}, c_{\ell\sigma}^+\} \rangle + \langle\langle [n_{\ell\bar{\sigma}} c_{\ell\sigma}, H], c_{\ell\sigma}^+ \rangle\rangle \quad (4.5.19.a)$$

and

$$\Gamma_{\ell k\sigma}^{\ell\ell} = \frac{1}{2\pi} \langle \{n_{\ell\bar{\sigma}} c_{\ell\sigma}, c_{k\sigma}^+\} \rangle + \langle\langle [n_{\ell\bar{\sigma}} c_{\ell\sigma}, H], c_{k\sigma}^+ \rangle\rangle. \quad (4.5.19.b)$$

We know that

$$\{n_{\ell\bar{\sigma}} c_{\ell\sigma}, c_{\ell\sigma}^+\} = n_{\ell\bar{\sigma}}, \quad \{n_{\ell\bar{\sigma}} c_{\ell\sigma}, c_{k\sigma}^+\} = 0, \quad (4.5.20)$$

$$[n_{\ell\bar{\sigma}} c_{\ell\sigma}, H] = n_{\ell\bar{\sigma}} [c_{\ell\sigma}, H] + c_{\ell\bar{\sigma}}^+ [c_{\ell\sigma}, H] c_{\ell\sigma} + [c_{\ell\bar{\sigma}}^+, H] c_{\ell\bar{\sigma}} c_{\ell\sigma}, \quad (4.5.21)$$

$$[c_{\ell\sigma}, H] = \epsilon_{\ell} c_{\ell\sigma} + U \cdot n_{\ell\bar{\sigma}} c_{\ell\sigma} + \sum_k^{\circ} V_{\ell k} c_{k\sigma}, \quad (4.5.22.a)$$

$$[c_{\ell\bar{\sigma}}, H] = \epsilon_{\ell} c_{\ell\bar{\sigma}} + U \cdot n_{\ell\sigma} c_{\ell\bar{\sigma}} + \sum_k^{\circ} V_{\ell k} c_{k\bar{\sigma}} \quad (4.5.22.b)$$

$$\text{and } [c_{\ell\bar{\sigma}}^+, H] = - \left[ \epsilon_{\ell} c_{\ell\bar{\sigma}}^+ + U \cdot n_{\ell\sigma} c_{\ell\bar{\sigma}}^+ + \sum_k^{\circ} V_{k\ell} c_{k\bar{\sigma}}^+ \right]. \quad (4.5.22.c)$$

Since  $n_{\ell\sigma}^2 = n_{\ell\sigma}$  the result of substitution is

$$[n_{\ell\bar{\sigma}} c_{\ell\sigma}, H] = (\epsilon_{\ell} + U) \cdot n_{\ell\bar{\sigma}} c_{\ell\sigma} + \sum_k^{\circ} V_{\ell k} (n_{\ell\bar{\sigma}} c_{k\sigma} + c_{\ell\bar{\sigma}}^+ c_{k\bar{\sigma}} c_{\ell\sigma}) - V_{k\ell} c_{k\bar{\sigma}}^+ c_{\ell\bar{\sigma}} c_{\ell\sigma}. \quad (4.5.23)$$

Applying this result to 4.5.19.a, b, we get

$$(\omega - \epsilon_{\ell} - U) \cdot \Gamma_{\ell\ell\sigma}^{\ell\ell} = \langle n_{\ell\sigma} \rangle / 2\pi + k^{\circ} \left[ V_{\ell k} (\Gamma_{k\ell\sigma}^{\ell\ell} + \Gamma_{\ell\ell\sigma}^{\ell k'}) - V_{k\ell} \Gamma_{\ell\ell\sigma}^{k\ell} \right] \quad (4.5.24.a)$$

$$(\omega - \epsilon_{\ell} - U) \cdot \Gamma_{\ell k\sigma}^{\ell\ell} = \sum_k^{\circ} \left[ V_{\ell k'} (\Gamma_{k'k\sigma}^{\ell\ell} + \Gamma_{\ell k\sigma}^{\ell k'}) - V_{k\ell} \Gamma_{\ell k\sigma}^{k\ell} \right]. \quad (4.5.24.b)$$

If we apply  $\Gamma_{\ell j \sigma}^{k \ell}$ ,  $\Gamma_{\ell j \sigma}^{\ell k}$ ,  $\Gamma_{k j \sigma}^{\ell \ell}$  into the equation of motion again, we would get the equation defining the higher order Green function. As Zubarev (1960) suggested, we should close the cycle of equation with some approximation, which factors the high order Green function into lower order Green function.<sup>89</sup>

Let us consider diagrammatic representation of all the two-particle Green function. We have



$$\Gamma_{\ell \ell \sigma}^{\ell \ell}(t)$$



$$\Gamma_{k \ell \sigma}^{\ell \ell}(t)$$

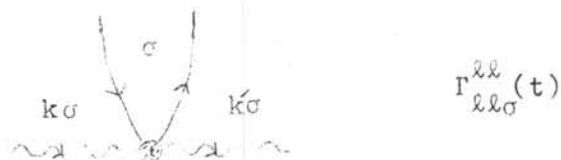


$$\Gamma_{\ell \ell \sigma}^{\ell k}(t)$$



$$\Gamma_{\ell \ell \sigma}^{k \ell}(t)$$

Similarly  $\Gamma_{\ell\ell k\sigma}^{\ell\ell}$ ,  $\Gamma_{kk\sigma}^{\ell\ell}$ ,  $\Gamma_{\ell k\sigma}^{\ell k'}$ ,  $\Gamma_{\ell k\sigma}^{k'\ell}$  can be represented by similar diagrams. As example



where  $\rightarrow$  and  $\sim\rightarrow$  are the electron propagators in impurity site and in metals.

In the Hartree-Fock approximation, we factor the two-particle Green function as following;

$$\Gamma_{\ell\ell\sigma}^{\ell\ell} \approx \langle n_{\ell\bar{\sigma}} \rangle \cdot G_{\ell\ell}^{\sigma}$$

To go beyond the Hartree-Fock approximation, Hubbard suggested the following;<sup>92</sup>

$$\begin{aligned} \Gamma_{k\ell\sigma}^{\ell\ell} &= \langle n_{\ell\bar{\sigma}} \rangle \cdot G_{k\ell}^{\sigma}, & \Gamma_{\ell\ell\sigma}^{\ell k} &= \langle c_{\ell\bar{\sigma}}^{\dagger} c_{k\bar{\sigma}} \rangle \cdot G_{\ell\ell}^{\sigma}, \\ \Gamma_{\ell\ell\sigma}^{k\ell} &= \langle c_{k\bar{\sigma}}^{\dagger} c_{\ell\bar{\sigma}} \rangle \cdot G_{\ell\ell}^{\sigma}, & \Gamma_{kk\sigma}^{\ell\ell} &= \langle n_{\ell\bar{\sigma}} \rangle \cdot G_{kk}^{\sigma}, \\ \Gamma_{\ell k\sigma}^{\ell k'} &= \langle c_{\ell\bar{\sigma}}^{\dagger} c_{k\bar{\sigma}} \rangle \cdot G_{\ell k}^{\sigma}, & \Gamma_{\ell k\sigma}^{k'\ell} &= \langle c_{k\bar{\sigma}}^{\dagger} c_{\ell\bar{\sigma}} \rangle \cdot G_{k\ell}^{\sigma}. \end{aligned}$$

This is something similar to Hartree-Fock approximation in that it average the interaction in the black box as an average function  $\langle c_{i\bar{\sigma}}^{\dagger} c_{j\bar{\sigma}} \rangle$ . In this way, the two-particle Green function  $\Gamma_{\ell\ell\sigma}^{\ell\ell}$ ,  $\Gamma_{\ell k\sigma}^{\ell\ell}$  and all single-particle Green functions

are obtained by making use the symmetric property of  $\langle c_{\ell\bar{\sigma}}^t c_{k\bar{\sigma}} \rangle = \langle c_{k\bar{\sigma}}^c c_{\ell\bar{\sigma}} \rangle$ .

4.5.24.a, b become

$$(\omega - \epsilon_{\ell} - U) \cdot \Gamma_{\ell\ell\sigma}^{\ell\ell} = \langle n_{\ell\bar{\sigma}} \rangle / 2\pi + \langle n_{\ell\bar{\sigma}} \rangle \cdot \Sigma_{k'} \cdot V_{\ell k'} G_{k'k\ell}^{\sigma}$$

and  $(\omega - \epsilon_{\ell} - U) \cdot \Gamma_{\ell k\sigma}^{\ell\ell} = \langle n_{\ell\bar{\sigma}} \rangle \cdot \Sigma_{k'} \cdot V_{\ell k'} G_{k'k\ell}^{\sigma}$  .

Applying 4.5.15.c,d to these equations, we have

$$(\omega - \epsilon_{\ell} - U) \cdot \Gamma_{\ell\ell\sigma}^{\ell\ell} = \frac{\langle n_{\ell\bar{\sigma}} \rangle}{2\pi} \cdot \left[ 1 + 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell}^{\sigma} \right]$$

and  $(\omega - \epsilon_{\ell} - U) \cdot \Gamma_{\ell k\sigma}^{\ell\ell} = \langle n_{\ell\bar{\sigma}} \rangle \cdot \Sigma_0 \cdot G_{\ell k}^{\sigma}$  ,

where  $\Sigma_0$  has been defined in 4.5.17. Thus

$$\Gamma_{\ell\ell\sigma}^{\ell\ell} = \frac{n_{\ell\bar{\sigma}}}{2\pi} \cdot \left[ \frac{1 + 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell}^{\sigma}}{(\omega - \epsilon_{\ell} - U)} \right] \quad (4.5.25.a)$$

and  $\Gamma_{\ell k}^{\ell\ell} = n_{\ell\bar{\sigma}} \cdot \Sigma_0 \cdot \left[ \frac{G_{\ell k}^{\sigma}}{(\omega - \epsilon_{\ell} - U)} \right]$  , (4.5.25.b)

where  $n_{\ell\bar{\sigma}} = \langle n_{\ell\bar{\sigma}} \rangle$ . If we put these result back into 4.5.16.a,b,

the single-particle Green functions are then given by

$$(\omega - \epsilon_{\ell} - \Sigma_0) \cdot G_{\ell\ell}^{\sigma} = \frac{1}{2\pi} \cdot \left[ 1 + \frac{U \cdot n_{\ell\bar{\sigma}} \cdot (1 + 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell}^{\sigma})}{(\omega - \epsilon_{\ell} - U)} \right] \quad (4.5.26.a)$$

and  $(\omega - \epsilon_{\ell} - \Sigma_0) \cdot G_{\ell k}^{\sigma} = \frac{U \cdot n_{\ell\bar{\sigma}} \cdot \Sigma_0 \cdot G_{\ell k}^{\sigma}}{(\omega - \epsilon_{\ell} - U)} + \frac{V_{\ell k}}{2\pi \cdot (\omega - \epsilon_{\ell})}$  . (4.5.26.b)



Rearranging the term, we get

$$\left\{ 1 - \Sigma_0 \cdot \left[ \frac{1}{(\omega - \epsilon_\ell)} + \frac{U \cdot n_{\bar{\sigma}}}{(\omega - \epsilon_\ell) \cdot (\omega - \epsilon_\ell - U)} \right] \right\} \cdot G_{\ell\ell}^\sigma = \frac{1}{2\pi} \cdot \left[ \frac{1}{(\omega - \epsilon_\ell)} + \frac{U \cdot n_{\bar{\sigma}}}{(\omega - \epsilon_\ell) \cdot (\omega - \epsilon_\ell - U)} \right]$$

$$\left\{ 1 - \Sigma_0 \cdot \left[ \frac{1 - n_{\bar{\sigma}}}{(\omega - \epsilon_\ell)} + \frac{n_{\bar{\sigma}}}{(\omega - \epsilon_\ell - U)} \right] \right\} \cdot G_{\ell\ell}^\sigma = \frac{1}{2\pi} \cdot \left[ \frac{1 - n_{\bar{\sigma}}}{(\omega - \epsilon_\ell)} + \frac{n_{\bar{\sigma}}}{(\omega - \epsilon_\ell - U)} \right] \cdot$$

Using the expression 4.5.10, we get

$$G_{\ell\ell}^\sigma(\omega) = \frac{G_{\ell\ell\sigma}^0(\omega)}{1 - 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell\sigma}^0(\omega)} \quad (4.5.27.a)$$

Similarly, we get

$$G_{\ell k}^\sigma(\omega) = \frac{V_{\ell k} \cdot G_{kk\sigma}^0(\omega)}{1 - 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell\sigma}^0(\omega)} \quad (4.5.27.b)$$

Applying these results back into the equation 4.5.15.c,d, we can obtain all the single-particle Green function.

The equation 4.5.27.a can be put in form of a Dyson's equation<sup>88</sup> by rewriting it as

$$G_{\ell\ell}^\sigma = G_{\ell\ell\sigma}^0 + G_{\ell\ell\sigma}^0 \cdot 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell\sigma}^0 + G_{\ell\ell\sigma}^0 \cdot 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell\sigma}^0 \cdot 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell\sigma}^0$$

$$+ G_{\ell\ell\sigma}^0 \cdot 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell\sigma}^0 \cdot 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell\sigma}^0 \cdot 2\pi \cdot \Sigma_0 \cdot G_{\ell\ell\sigma}^0 + \dots \quad (4.5.28)$$

The Hubbard approximation goes only slightly beyond to the Hartree-Fock, but leads a significant change in the physical interpretation.

#### 4.6 The density distribution of $\ell$ -state.

The density of states function at impurity site is defined as a projection onto the sub-space  $\{|\ell\sigma\rangle\}$ , i.e.

$$\rho_{\ell\ell}^{\sigma}(\omega) = \sum_m \delta(\epsilon_m - \omega) \cdot |\langle m\sigma | \ell\sigma \rangle|^2 \quad (4.6.1)$$

It can be related to double-time Green function by the relation<sup>89</sup>

$$\begin{aligned} \rho_{\ell\ell}^{\sigma}(\omega) &= i \cdot \lim_{s \rightarrow 0^+} \left[ G_{\ell\ell}^{\sigma}(\omega + is) - G_{\ell\ell}^{\sigma}(\omega - is) \right] \quad (4.6.2) \\ &= i \cdot \lim_{s \rightarrow 0^+} \left[ \frac{G_{\ell\ell\sigma}^{\circ}(\omega + is)}{1 - 2\pi \cdot (\Lambda_{\circ} - i\Delta_{\circ}) \cdot G_{\ell\ell\sigma}^{\circ}(\omega + is)} \right. \\ &\quad \left. - \frac{G_{\ell\ell\sigma}^{\circ}(\omega - is)}{1 - 2\pi \cdot (\Lambda_{\circ} + i\Delta_{\circ}) \cdot G_{\ell\ell\sigma}^{\circ}(\omega - is)} \right] , \end{aligned}$$

where the self-energy  $\Sigma_{\circ}$  is splitted into two parts the absorption ( $\Lambda_{\circ}$ ) and dispersion ( $\Delta_{\circ}$ ) part. We then have

$$\Sigma_{\circ} = \Lambda_{\circ} - i\Delta_{\circ} ,$$

where

$$\begin{aligned} \Delta_{\circ} &= \lim_{s \rightarrow 0^+} \sum_k |V_{\ell k}|^2 / (\omega - \epsilon_k)^2 + s^2 \\ &= \pi \cdot \sum_k |V_{\ell k}|^2 \cdot \delta(\omega - \epsilon_k) \quad (4.6.3.a) \end{aligned}$$

and

$$\Lambda_{\circ} = \frac{1}{\pi} \cdot \text{P} \int d\omega' \cdot \Delta_{\circ}(\omega') / (\omega - \omega') \quad (4.6.3.b)$$

The integral  $\int P d\omega$  is understood to be Cauchy principle integral. Since  $G_{\ell\ell\sigma}^{\circ}$  has discretized pole of zero width, we have  $G_{\ell\ell\sigma}^{\circ}(\omega - is) = G_{\ell\ell\sigma}^{\circ}(\omega + is)$  in the limit of  $s \rightarrow 0^+$ . Thus

$$\begin{aligned} \rho_{\ell\ell}^{\sigma}(\omega) &= G_{\ell\ell\sigma}^{\circ}(\omega) \cdot \left[ \frac{2 \cdot \Delta_{\circ} \cdot 2\pi \cdot G_{\ell\ell\sigma}^{\circ}(\omega)}{(1 - 2\pi \cdot \Lambda_{\circ} \cdot G_{\ell\ell\sigma}^{\circ}(\omega))^2 + (\Delta_{\circ} \cdot G_{\ell\ell\sigma}^{\circ}(\omega))^2} \right] \\ &= \frac{\Delta_{\circ}/\pi}{((2\pi \cdot G_{\ell\ell\sigma}^{\circ}(\omega))^{-1} - \Lambda_{\circ})^2 + \Delta_{\circ}^2} \quad (4.6.4) \end{aligned}$$

Equation 4.6.4 shows the relationships of  $\rho_{\ell\ell}^{\sigma}(\omega)$  and  $G_{\ell\ell\sigma}^{\circ}(\omega)$ ,  $\Lambda_{\circ}$  and  $\Delta_{\circ}$ . By making different approximation for  $G_{\ell\ell\sigma}^{\circ}(\omega)$ , we will get the different expression for  $\rho_{\ell\ell}^{\sigma}(\omega)$ , i.e. in Hartree-Fock approximation

$$\rho_{\ell\ell}^{\sigma}(\omega) = \frac{\Delta_{\circ}/\pi}{(\omega - \epsilon_{\ell\sigma} - \Lambda_{\circ})^2 + \Delta_{\circ}^2}, \quad (4.6.5.a)$$

while in the Hubbard approximation

$$\rho_{\ell\ell}^{\sigma}(\omega) = \frac{\Delta_{\circ}/\pi}{\left[ \frac{(\omega - \epsilon_{\ell}) \cdot (\omega - \epsilon_{\ell} - U)}{(\omega - \epsilon_{\ell} - U \cdot (1 - n_{\sigma}))} - \Lambda_{\circ} \right]^2 + \Delta_{\circ}^2} \quad (4.6.5.b)$$

Generally  $\Lambda_{\circ}$ ,  $\Delta_{\circ}$  are treated as parameters which are varied in order to obtain an idea of the behavior of the density of states. Some numerical results are shown graphically in Fig. 4.6.1.a, b.

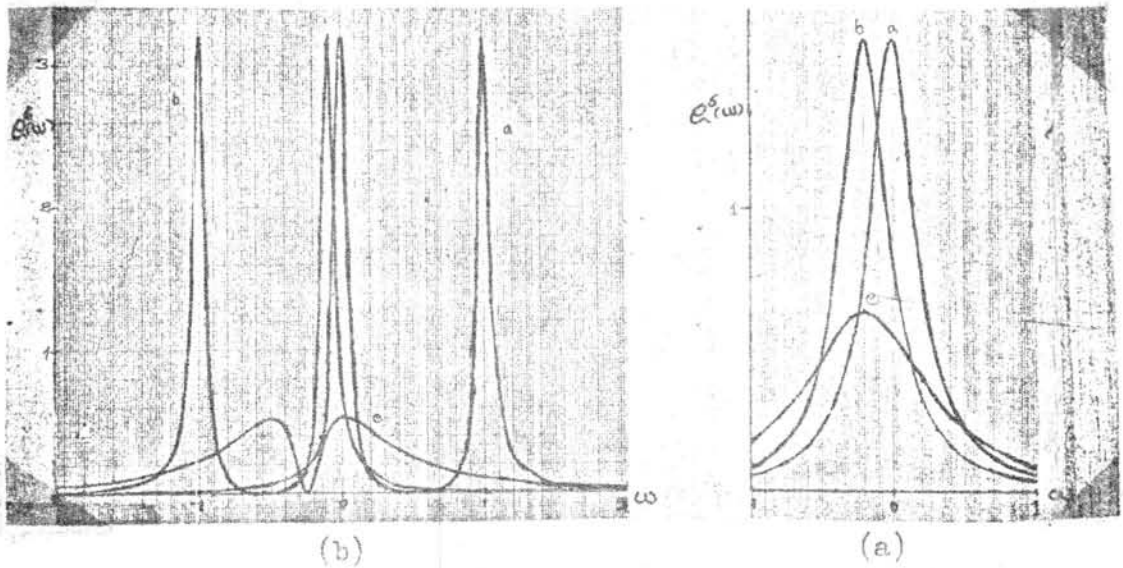


Fig.4.6.1: The density of state function at impurity site in

(a) Hartree-Fock approximation,  $\epsilon_{j\delta} + \lambda_0 \quad \Delta_0$

a :	0.0	0.2
b :	-0.2	0.2
c :	-0.2	0.5

(b) Hubbard-Newson approximation,

	$\epsilon_l$	$U$	$\lambda_0$	$\Delta_0$	$n_\delta$
a :	0.0	1.0	0.00	0.1	0.5
b :	-1.0	0.9	0.01	0.1	0.5
c :	-0.5	0.5	0.02	0.6	0.5

#### 4.7 Self-consistent condition for localized moment.

In the previous section we obtained 4.6.4, which is general expression for the density of states for a system containing  $\ell$ -admixture with the continuum states of energy  $\epsilon_k$ .

In order to determine the number of electrons of a given spin  $\sigma$ , we intergrate 4.6.4 up to  $\epsilon_F$ .

$$\text{Thus } \langle n_{\ell\sigma} \rangle = \int_{-\infty}^{\epsilon_F} d\omega \cdot \rho_{\ell\ell}^{\sigma}(\omega) \quad (4.7.1)$$

$$= \int_{-\infty}^{\epsilon_F} d\omega \cdot \frac{\Delta_0/\pi}{\left[ (2\pi \cdot G_{\ell\ell\sigma}^0(\omega))^{-1} - \Lambda_0 \right]^2 + \Delta_0^2} \quad (4.7.2)$$

This expression is quite general. We will now study the formation of localized moment under Hartree-Fock approximation. Equation 4.7.2 becomes

$$n_{\sigma} = \int_{-\infty}^{\epsilon_F} d\omega \cdot \frac{\Delta_0/\pi}{(\omega - \epsilon_{\ell} - \Lambda_0)^2 + \Delta_0^2} \quad (4.7.3)$$

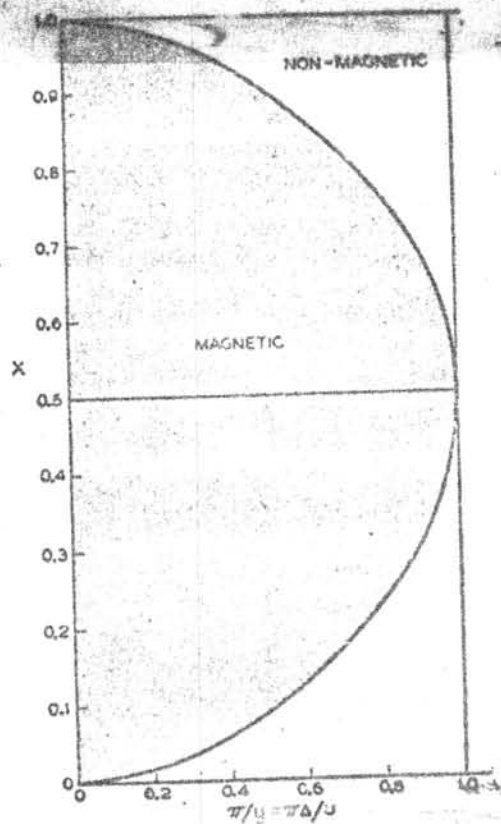
Treating  $\Lambda_0, \Delta_0$  as parameters, 4.7.3 can be intergrated to give

$$n_{\sigma} = \frac{1}{\pi} \cdot \cot^{-1} \left[ \frac{\epsilon_F - \epsilon_{\ell} - \Lambda_0}{\Delta_0} \right] \quad (4.7.4)$$

$$\text{Defining } y = U/\Delta_0 \quad (4.7.5)$$

$$\text{and } x = (\epsilon_F - \epsilon_{\ell} - \Lambda_0)/U,$$

$$\text{we get } n_{\sigma} = \frac{1}{\pi} \cdot \cot^{-1} y(x - n_{\sigma}) \quad (4.7.6)^{38}$$



Regions of magnetic and nonmagnetic behavior.  
 Curve gives  $x_c$  vs  $z/y_c = T\Delta/U$ .

Fig. 4.7.1 <sup>38</sup>

This shows explicitly the dependent of  $n_{\sigma}$  on  $n_{\bar{\sigma}}$ , or alternately  $n_{\bar{\sigma}}$  on  $n_{\sigma}$ .

As already mentioned, there are two processes, the covalent admixing process and the intra-atomic Coulomb interaction of opposite spin, competing against each other. The larger the intra-atomic Coulomb interaction, the greater the possibility of the localized moment existing. The width of the virtual state indicates the destruction of the former process. Thus large  $y$  corresponds to the magnetic case, while small  $y$  corresponds to the non-magnetic case. At one point we have  $y_c = U_c / \Delta_o^c$ , the changing point of these two cases. However, the competition of the two processes can not be simply represented by only  $U$  and  $\Delta_o$ , it also is dependent on the absorption part  $\Lambda_o$  of the self-energy. There also exists  $x_c = (\epsilon_F - \epsilon_{\ell} - \Lambda_o^c) / U_c$  at the changing point. Generally speaking, there exists the boundary curve between the two regions, the magnetic and non-magnetic, requires as show in Fig.4.7.1,b An analytic expression for the curve is difficult to obtain, even in the Hartree-Fock approximation.

Let us now consider the approximation which goes beyond the Hartree-Fock, for example Hubbard approximation. Putting the expression 4.6.5.b into 4.7.1, we get

$$n_o = \int_{-\infty}^{\epsilon_F} d\omega \frac{\Delta_o / \pi}{\left[ \frac{(\omega - \epsilon_{\ell}) \cdot (\omega - \epsilon_{\ell} - U)}{(\omega - \epsilon_{\ell} - U) \cdot (1 - n_{\bar{\sigma}})} - \Lambda_o \right]^2 + \Delta_o^2} \quad (4.7.7)$$

This can be evaluated if we treat  $\Lambda_0$  and  $\Delta_0$  as parameters. This has been shown by Hewson to give a complicate result.<sup>93</sup> However, the dependent of  $n_\sigma$  on  $n_{\bar{\sigma}}$  is similar to that of the previous case. The general methods of finding the solution is to solve the self-consistent condition

$$n_\uparrow = N(U, \epsilon_F, \Lambda_0^F, \Delta_0^F, n_\downarrow) \quad (4.7.8.a)$$

and

$$n_\downarrow = N(U, \epsilon_F, \Lambda_0^F, \Delta_0^F, n_\uparrow) \quad (4.7.8.b)$$

These two equations can be solved simultaneously and yield three solutions, two of which are magnetic, while the third is non-magnetic. The single solution exists for some special value of parameters. This single solution corresponds to the non-magnetic case. If the system have three solutions, only two of them are the ground state solutions and the system is magnetic.