

## CHAPTER V

### THE CORRELATION EFFECT AND GENERALIZATION OF BM APPROXIMATION

Similar to the bulk impurity, the correlation effect is also important in chemisorption. Brenig and Schönhammer (1974)<sup>96</sup> have discussed the correlation effect in H-chemisorption and their calculation is found to agree with the exact computer calculation by Schrieffer and Einstein for one dimensional chain of three metal atoms plus an adatom containing four electrons. This effect was also discussed from different point of view by Bell and Madhukar (1975-1976).<sup>97,98</sup> BM worked out the problem with the use of microscopic Hamiltonian, first introduced by Madhukar (IBM Research Report No RC5413, unpublished). Their result is successful in showing the physical content in the Green function explicitly. In contrast to BM, we will use Anderson Hamiltonian (BM treated this as a limit of their Hamiltonian) for the reason that all parameters in the Hamiltonian can be evaluated from experimental data, which then requires no self-consistent calculation. The Anderson phenomenological Hamiltonian has an advantage of being simple and contains all important physical properties, and the microscopic structure of the parameters can be separated to be another problem which may or may not be the same as BM. In our view point, BM's Hamiltonian is the special approximation to the Anderson Hamiltonian.

BM decoupling scheme is the special case of our generalized BM decoupling scheme, shown in 5.3. The comparison of HH, BM, and BS will be discussed under the use of the matrix formalism. The formalism is defined and applied to solve the single particle Green function in 5.1. The HF approximation is recalculated to show the power of the formalism and the detail discussion of this approximation for H-chemisorption is also given.

#### 5.1 The matrix formalism for solving single particle Green functions.

In both impurity and chemisorption problem, we have two sets of state vectors,  $\{|l\sigma\rangle\}$  and  $\{|k\sigma\rangle\}$ , so that we can divide the matrix representation of all measurements of spin  $\sigma$  into block form as we have discussed in appendix D.

From 4.5.15.a,b,c,d, we can write the system of equations of motion for single particle Green function into matrix form as

$$\frac{1}{2\pi} \cdot g_{\sigma}^{-1} \cdot G_{\sigma} = \frac{1}{2\pi} \cdot I_{\sigma} + U \cdot T_{\sigma} + V_{\sigma} \cdot G_{\sigma} \quad (5.1.1)$$

Here  $g_{\sigma}$  is the single particle Green function matrix for the isolated, non-interacting, system and is defined as follows

$$g_{\sigma} = \begin{pmatrix} g_{11} & 0 \\ 0 & g_{22} \end{pmatrix}, \quad (5.1.2)$$

where  $g_{11} = \frac{1/2\pi}{\omega - \epsilon_l}$

and  $g_{22}$  is diagonalized matrix having matrix element  $(g_{22})_{kk'}$

as follow

$$(g_{22})_{kk'} = \frac{\delta_{kk'}}{\omega - \epsilon_k} / 2\pi$$

The single particle Green function of the interacting system is represented by matrix  $G_\sigma$  defined as follow

$$G_\sigma = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix}, \quad (5.1.3)$$

where  $G_{11}$ ,  $G_{12}$ ,  $G_{21}$ ,  $G_{22}$  are defined similar to  $D_2$  in appendix D. The two particle Green function, associated with the correlation potential  $U$ , has the matrix representation

$$T_\sigma = \begin{pmatrix} T_{11} & T_{12} \\ 0_{21} & 0_{22} \end{pmatrix}, \quad (5.1.4)$$

which has matrix elements  $T_{11}$  and  $(T_{12})_{lk}$  as follow

$$T_{11} = \Gamma_{ll\sigma}^{ll}(\omega) = \langle\langle n_{l\sigma} c_{l\sigma}, c_{l\sigma}^\dagger \rangle\rangle$$

$$\text{and } (T_{12})_{lk} = \Gamma_{lk\sigma}^{ll}(\omega) = \langle\langle n_{l\sigma} c_{l\sigma}, c_{k\sigma}^\dagger \rangle\rangle.$$

In 5.1.4 we have shown explicitly that

$$(T_{21})_{k\ell} = 0 \quad \text{and} \quad (T_{22})_{kk'} = 0 \quad .$$

The admixing coefficient is given in matrix form as

$$V_{\sigma} = \begin{bmatrix} 0_{11} & V_{12} \\ V_{21} & 0_{22} \end{bmatrix}, \quad (5.1.5)$$

where  $(V_{12})_{\ell k} = V_{\ell k}$  and  $(V_{21})_{k\ell} = V_{k\ell}$  .

The  $V_{\ell k}$  and  $V_{k\ell}$  have previously been defined (see Chapter IV).

Since  $\Gamma_{\ell\ell\sigma}^{\ell\ell}$  and  $\Gamma_{\ell k\sigma}^{\ell\ell}$  can be solved by direct

decoupling or by inserting it into a new set of equations of motion and then decoupling the higher order Green function, we propose that  $T_{\sigma}$  can be written as function of  $G_{\sigma}$  as follow

$$T_{\sigma} = \frac{1}{2\pi} \cdot A_{\sigma} + B_{\sigma} \cdot G_{\sigma} \quad . \quad (5.1.6)$$

Here  $A_{\sigma}$  and  $B_{\sigma}$  are functions of matrix, which depend directly on the decoupling scheme, defined to be of type III block form. Substituting 5.1.6 into 5.1.1, we have

$$(I_{\sigma} - 2\pi \cdot g_{\sigma} V_{\sigma} - 2\pi \cdot U \cdot g_{\sigma} \cdot B_{\sigma}) \cdot G_{\sigma} = g_{\sigma} \cdot (I_{\sigma} + U \cdot A_{\sigma}) \quad . \quad (5.1.7)$$

We further define

$$K_{\sigma} = \begin{bmatrix} 1-2\pi \cdot U \cdot \epsilon_{11} B_{11} & 0_{12} \\ 0_{21} & I_{22} \end{bmatrix} \text{ and } L_{\sigma} = 2\pi \cdot \begin{bmatrix} 0_{11} & \epsilon_{11} V_{12} + U \cdot \epsilon_{11} B_{12} \\ \epsilon_{22} V_{21} & 0_{22} \end{bmatrix} \quad (5.1.8)$$

The equation 5.1.7 can be rewritten as

$$(K_{\sigma} - L_{\sigma}) \cdot G_{\sigma} = \epsilon_{\sigma} \cdot (I_{\sigma} + U \cdot A_{\sigma}) \cdot$$

Multiplying both sides by the inverse of  $K_{\sigma}$ , and then by the inverse of  $(I_{\sigma} - K_{\sigma}^{-1} \cdot L_{\sigma})$ , we get

$$G_{\sigma} = (I_{\sigma} - K_{\sigma}^{-1} \cdot L_{\sigma}) \cdot K_{\sigma}^{-1} \cdot \epsilon_{\sigma} \cdot (I_{\sigma} + U \cdot A_{\sigma}) \quad (5.1.9)$$

From 5.1.8, we find that

$$K_{\sigma}^{-1} \cdot L_{\sigma} = 2\pi \cdot \begin{bmatrix} 0_{11} & \frac{\epsilon_{11} V_{12} + U \cdot \epsilon_{11} B_{12}}{1-2\pi \cdot U \cdot \epsilon_{11} B_{11}} \\ \epsilon_{22} V_{21} & 0_{22} \end{bmatrix}, \quad (5.1.10)$$

which is type II matrix. If we define

$$\lambda = (K_{\sigma}^{-1} \cdot L_{\sigma})_{12} (K_{\sigma}^{-1} \cdot L_{\sigma})_{21},$$

we get

$$\lambda = \frac{(2\pi)^2 \cdot \epsilon_{11} V_{12} \epsilon_{22} V_{21} + U \cdot \epsilon_{11} B_{12} \epsilon_{22} V_{21}}{1 - 2\pi \cdot U \cdot \epsilon_{11} B_{11}}, \quad (5.1.11)$$

Equation 5.1.9 can then be written as

$$G_{\sigma} = \left[ K_{\sigma}^{-1} \cdot \epsilon_{\sigma} + \frac{K_{\sigma}^{-1} \cdot L_{\sigma} \cdot K_{\sigma}^{-1} \cdot \epsilon_{\sigma} + K_{\sigma}^{-1} \cdot L_{\sigma} \cdot K_{\sigma}^{-1} \cdot L_{\sigma} \cdot K_{\sigma}^{-1} \cdot \epsilon_{\sigma}}{1 - \lambda} \right] \cdot (I_{\sigma} + U \cdot A_{\sigma}) \quad (5.1.12)$$

$$\text{Here } K_{\sigma}^{-1} \cdot \epsilon_{\sigma} = \begin{pmatrix} \epsilon_{11}/(1-2\pi \cdot U \cdot \epsilon_{11} B_{11}) & 0_{12} \\ 0_{21} & \epsilon_{22} \end{pmatrix}, \quad (5.1.13.a)$$

$$K_{\sigma}^{-1} \cdot L_{\sigma} \cdot K_{\sigma}^{-1} \cdot \epsilon_{\sigma} = \frac{2\pi}{1-2\pi \cdot U \cdot \epsilon_{11} B_{11}} \cdot \begin{pmatrix} 0_{11} & \epsilon_{11} V_{12} \epsilon_{22} + U \cdot \epsilon_{11} B_{12} \epsilon_{22} \\ \epsilon_{22} V_{21} \epsilon_{11} & 0_{22} \end{pmatrix}. \quad (5.1.13.b)$$

$$K_{\sigma}^{-1} \cdot L_{\sigma} \cdot K_{\sigma}^{-1} \cdot L_{\sigma} \cdot K_{\sigma}^{-1} \cdot \epsilon_{\sigma} = \frac{1}{1-2\pi \cdot U \cdot \epsilon_{11} B_{11}} \cdot \begin{pmatrix} \lambda \cdot \epsilon_{11} & 0_{12} \\ 0_{21} & (2\pi)^2 \cdot (\epsilon_{22} V_{21} \epsilon_{11} V_{12} \epsilon_{22} + U \cdot \epsilon_{22} V_{21} \epsilon_{11} B_{12} \epsilon_{22}) \end{pmatrix} \quad (5.1.13.c)$$

This result shows that we could find all single particle Green function, i.e.

$$G_{11} = \frac{\epsilon_{11}}{1-2\pi \cdot U \cdot \epsilon_{11} B_{11}} \cdot \frac{1+U \cdot \Lambda_{11}}{1-\lambda}, \quad (5.1.14.a)$$

$$G_{22} = \epsilon_{22} + \frac{(2\pi)^2 \cdot (\epsilon_{22} V_{21} \epsilon_{11} \cdot (U \cdot \Lambda_{12} + (V_{12} + U \cdot B_{12}) \cdot \epsilon_{22}))}{(1-2\pi \cdot U \cdot \epsilon_{11} B_{11}) \cdot (1-\lambda)}, \quad (5.1.14.b)$$

$$G_{12} = \frac{\epsilon_{11}}{1-2\pi \cdot U \cdot \epsilon_{11} B_{11}} \cdot \frac{U \cdot \Lambda_{12} + (V_{12} + U \cdot B_{12}) \cdot \epsilon_{22}}{1-\lambda}, \quad (5.1.14.c)$$

$$\text{and } G_{21} = \frac{\epsilon_{22} V_{21} \epsilon_{11}}{1-2\pi \cdot U \cdot \epsilon_{11} B_{11}} \cdot \frac{1+U \cdot \Lambda_{11}}{1-\lambda} \quad (5.1.14.d)$$

## 5.2 Hartree-Fock approximation<sup>11,12,37,38,52</sup>

This approximation has been used to consider  $G_{\ell\ell}^{\sigma}(\omega)$  for impurity in metals as shown in 4.6.5.a. This result and all other single particle Green function will be solved simultaneously by the matrix formalism, which has been proposed in appendix D and the previous section. Since we decouple

$$\Gamma_{\ell j\sigma}^{\ell\ell} = n_{\sigma} \cdot G_{\ell j}^{\sigma} \quad , \quad (5.2.1)$$

or we have the matrix element  $(A_{11})_{\ell\ell} = (A_{12})_{\ell k} = (B_{12})_{\ell k} = 0$  and  $(B_{11})_{\ell\ell} = n_{\sigma}$ . From 5.1.11, we have

$$\lambda = \frac{(2\pi)^2 \cdot \epsilon_{11} V_{12} \epsilon_{22} V_{21}}{1 - 2\pi \cdot U \cdot \epsilon_{11} \cdot n} \quad , \quad (5.2.2)$$

Therefore 5.1.13.a, b, c and d become

$$G_{11} = \frac{\epsilon_{11}}{1 - 2\pi \cdot U \cdot \epsilon_{11} \cdot n - (2\pi)^2 \cdot \epsilon_{11} V_{12} \epsilon_{22} V_{21}} \quad , \quad (5.2.3.a)$$

$$G_{22} = \epsilon_{22} + \frac{(2\pi)^2 \cdot \epsilon_{22} V_{21} \epsilon_{11} V_{12} \epsilon_{22}}{1 - 2\pi \cdot U \cdot \epsilon_{11} \cdot n - (2\pi)^2 \cdot \epsilon_{11} V_{12} \epsilon_{22} V_{21}} \quad , \quad (5.2.3.b)$$

$$G_{12} = \frac{\epsilon_{11} V_{12} \epsilon_{22}}{1 - 2\pi \cdot U \cdot \epsilon_{11} \cdot n - (2\pi)^2 \cdot \epsilon_{11} V_{12} \epsilon_{22} V_{21}} \quad . \quad (5.2.3.c)$$

$$G_{21} = \frac{\epsilon_{22} V_{21} \epsilon_{11}}{1 - 2\pi \cdot U \cdot \epsilon_{11} \cdot n - (2\pi)^2 \cdot \epsilon_{11} V_{12} \epsilon_{22} V_{21}} \quad . \quad (5.2.3.d)$$

a)  $\epsilon_{\ell\sigma}$  lies outside the band. There is then a solution  $\omega = \omega_{\ell}$  outside the band where  $\Delta(\omega) = 0$ . As there can not be propagated inside the metal, the state must be localized near the adsorbed atom. It is basically the adatom energy level  $\epsilon_{\ell\sigma}$  shifted slightly by the interaction with the metal.

b)  $\epsilon_{\ell\sigma}$  lies in the band. There is a solution  $\omega = \omega_v$  in the band, where  $\Delta \neq 0$ . The adsorbate density of state is now approximately

$$\rho_{\ell}^{\sigma} \approx \frac{\pi^{-1} \cdot \Delta}{(\omega - \omega_v)^2 + \Delta^2} \quad \text{for } \omega \approx \omega_v \quad (5.2.6)$$

This corresponds to the virtual state, which has a finite life time  $\tau = \Delta^{-1}$ . This life time becomes longer as the chemisorption becomes weaker.

In strong chemisorption limit, if  $\epsilon_{\ell\sigma}$  lies outside the band, the situation is the same as the case (a) in the weak chemisorption. However, the situation would be different if  $\epsilon_{\ell\sigma}$  lies inside the band.

c)  $\epsilon_{\ell\sigma}$  lies in the band with a pair of solutions the band. This situation resembles the molecular case, namely that the adsorbate is forming surface molecule. The states are localized in neighbourhood of the adatom, and so are interpreted as being a pair of bonding (the lower state) and anti-bonding (the upper state), due to the coupling of  $\epsilon_{\ell\sigma}$  with the metal band.



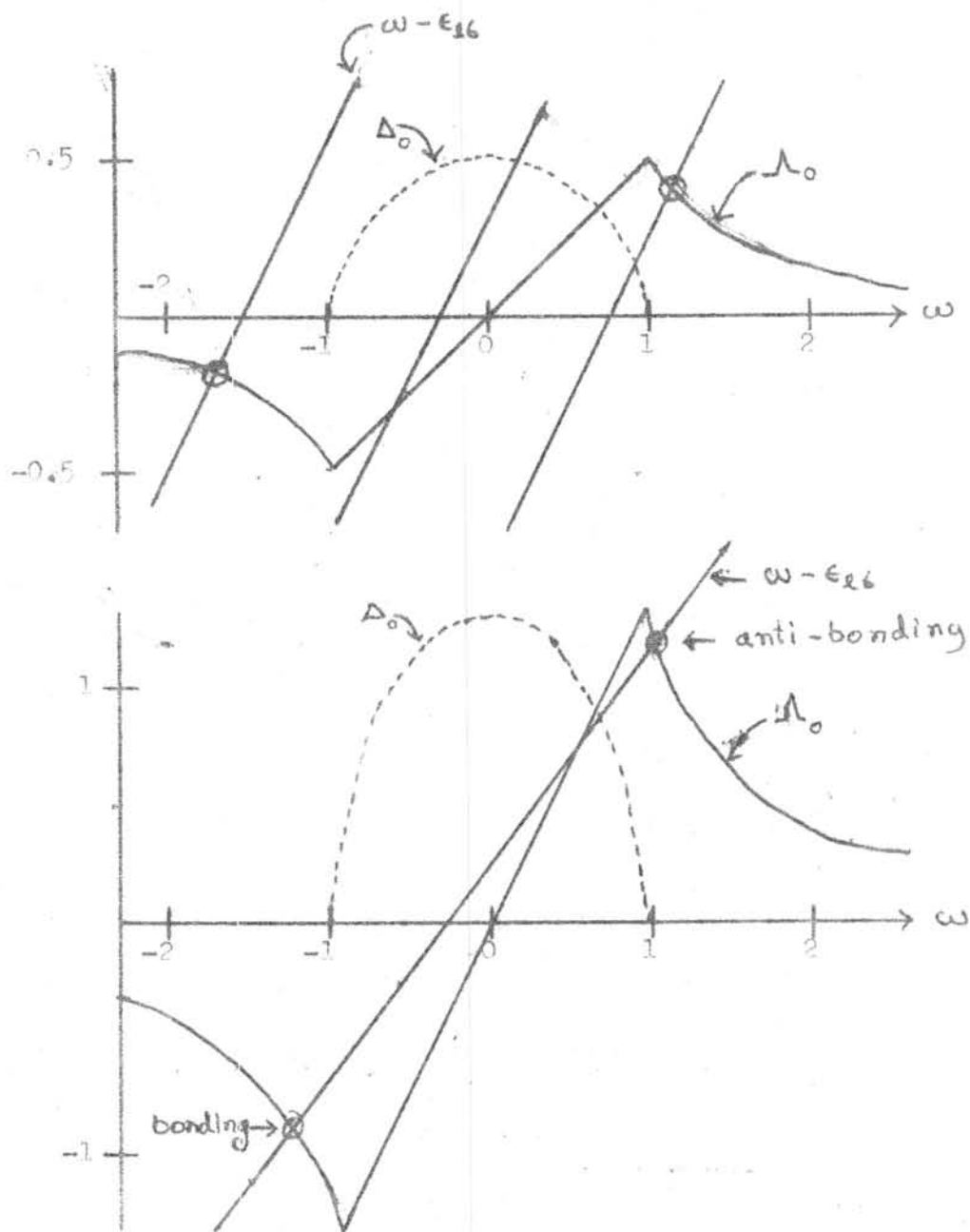


Fig. 5.2.1 : Semi-elliptical  $\Delta_0(\omega)$  with Hilbert transformation  $\Lambda_0(\omega)$ .<sup>37</sup>

Here we have combined  $\epsilon_{\ell}$  with the Coulomb shift  $Un_{\bar{\sigma}}$  to give  $\epsilon_{\ell\sigma}$  and self-energy of admixing process is

$$\Sigma_{\sigma}(\omega) = 2\pi \cdot V_{12} g_{22} V_{21} ,$$

which is equivalent to that defined in 4.5.17, called chemisorption function. Thus

$$\rho_{\ell}^{\sigma}(\omega) = \frac{\pi^{-1} \cdot \Delta(\omega)}{(\omega - \epsilon_{\ell\sigma} - \Lambda(\omega))^2 + \Delta^2(\omega)} , \quad (5.2.4)$$

where  $\Delta(\omega)$  and  $\Lambda(\omega)$  are defined in 4.6.3.a and b, and are studied in detail in appendix F. For infinitesimally small  $\Delta(\omega)$ , we know that  $\rho_{\ell}^{\sigma}(\omega)$  becomes  $\delta$ -function. In the absence of adsorbate-substrate interaction,  $V_{\ell k} = 0$ , the adsorbate level should be sharp. With this interaction, the adsorbate density of states  $\rho_{\ell}^{\sigma}(\omega)$  is shifted broadened, and further distorted due to the presence of the  $\Delta(\omega)$ ,  $\Lambda(\omega)$ .

To discuss the chemisorption localized state<sup>52</sup>, we must find the solution of

$$\omega - \epsilon_{\ell\sigma} - \Lambda(\omega) = 0 \quad (5.2.5)$$

In weak chemisorption limit  $\Delta(\omega)$  is small in comparison to the band width. In this situation there are two obvious cases to be considered :

The problem can not be treated properly until self-consistency has been achieved. The self consistency is given by

$$\begin{aligned} N(n_{\bar{\sigma}}) &= \frac{1}{\pi} \int_{-\infty}^{\epsilon_F} d\omega \cdot \rho_{\ell}^{\sigma}(\omega, \epsilon_{\ell\sigma}(n_{\bar{\sigma}})) \\ &= \frac{1}{\pi} \int_{-\infty}^{\epsilon_F} d\omega \cdot \rho_{\ell}^{\sigma}(\omega, \epsilon_{\ell\sigma}(n_{\bar{\sigma}})) + \langle n_{\ell\sigma} \rangle_{\text{localized}}, \quad (5.2.7) \end{aligned}$$

where the second term is the number of electrons occurring localized state which has energy level lying below the band. This term comes directly from the  $\delta$ -function integration. The number of localized electrons is given by Newns<sup>37</sup> with the use of Hurley<sup>99</sup> theorem that

$$\langle n_{\ell\sigma} \rangle_{\text{loc.}} = \left. \frac{\partial \omega}{\partial \epsilon} \right|_{\ell\sigma} \Big|_{\omega_{\ell}} = (1 - I'(\omega))^{-1}. \quad (5.2.8)$$

The self-consistent condition is achieved in the same way as discussed in chapter IV.

### 5.3 BM decoupling scheme and its generalization on Anderson Hamiltonian.

BM have introduced the microscopic Hamiltonian for describing the chemisorption of H on transition metal in site representation.<sup>97,98</sup> Their Hamiltonian has been shown to be equivalent to Anderson Hamiltonian in some limit. We suggest that it would be better to use BM-decoupling



scheme on Anderson Hamiltonian directly. We treat all the parameters in the Hamiltonian as being a part of different problem.

Let us go back to the equation of motion of  $\Gamma_{\ell\ell\sigma}^{\ell\ell}$  and  $\Gamma_{\ell k\sigma}^{\ell\ell}$  given by equations 4.5.24.a and b. Substituting all the two particle Green functions into the equation of motion again, we have

$$\Gamma_{kj\sigma}^{\ell\ell} = \frac{n_{\bar{\sigma}}}{2\pi} \delta_{kj} + \epsilon_k \cdot \Gamma_{kj}^{\ell\ell} + V_{k\ell} \cdot \Gamma_{\ell j}^{\ell\ell} + \sum_{k'} (V_{\ell k'} \cdot \Gamma_{kj\sigma}^{\ell k'} - V_{k\ell} \cdot \Gamma_{k'j\sigma}^{\ell\ell}), \quad (5.3.1.a)$$

$$\begin{aligned} \Gamma_{\ell j\sigma}^{\ell k} &= \frac{n_{\bar{\sigma}}}{2\pi} \delta_{\ell j} + \epsilon_k \cdot \Gamma_{\ell j\sigma}^{\ell k} + V_{k\ell} \cdot \Gamma_{\ell j\sigma}^{\ell\ell} + U \cdot \langle\langle (n_{\ell\bar{\sigma}} - n_{\ell\sigma}) c_{\ell\bar{\sigma}}^\dagger c_{k\bar{\sigma}} c_{\ell\sigma}, c_j^\dagger \rangle\rangle \\ &+ \sum_{k'} (V_{\ell k'} \cdot \Gamma_{k'j\sigma}^{\ell k} - V_{k\ell} \cdot \Gamma_{\ell j\sigma}^{kk'}) \quad , \quad (5.3.1.b) \end{aligned}$$

$$\begin{aligned} \Gamma_{\ell j\sigma}^{k\ell} &= \frac{n_{\bar{\sigma}}}{2\pi} \delta_{\ell j} - \epsilon_k \cdot \Gamma_{\ell j\sigma}^{k\ell} - V_{\ell k} \cdot \Gamma_{\ell j\sigma}^{\ell\ell} + 2\epsilon_{\ell} \cdot \Gamma_{\ell j\sigma}^{k\ell} + \\ &+ U \cdot \langle\langle (n_{\ell\bar{\sigma}} + n_{\ell\sigma}) c_{k\bar{\sigma}}^\dagger c_{\ell\bar{\sigma}} c_{\ell\sigma}, c_j^\dagger \rangle\rangle + \sum_{k'} V_{\ell k'} \cdot (\Gamma_{\ell j}^{kk'} + \Gamma_{k'j}^{k\ell}) \quad (5.3.1.c) \end{aligned}$$

BM have used the following decoupling scheme for the three particle Green function

$$\langle\langle (n_{\ell\bar{\sigma}} - n_{\ell\sigma}) c_{\ell\bar{\sigma}}^\dagger c_{k\bar{\sigma}} c_{\ell\sigma}, c_j^\dagger \rangle\rangle = 0 \quad ,$$

and

$$\langle\langle (n_{\ell\bar{\sigma}} + n_{\ell\sigma}) c_{k\bar{\sigma}}^\dagger c_{\ell\bar{\sigma}} c_{\ell\sigma}, c_j^\dagger \rangle\rangle = \Gamma_{\ell j\sigma}^{k\ell} \quad ,$$

which were not pointed out explicitly in their paper. We note that this approximation is possible only if the system has nearly zero magnetic moment. This corresponds to the case that  $U/\Delta < U_c/\Delta_c$

(see section 4.7). BM pointed out that their approximation was

applicable only to the case that  $V_{\ell k}$  is small.<sup>98,100,101</sup> This implies that  $\Delta$  is small, and then  $U$  is also small since it is less than  $\Delta \cdot U_c / \Delta_c$ , where we know that  $U_c / \Delta_c$  is not large. Since in the H-chemisorption problem  $U$  is not small, many authors have suggested that its value must go to infinity. There is no reason to believe that the BM decoupling is correct.

Let us define

$$m_{\ell\bar{\sigma}} = n_{\ell\bar{\sigma}} - n_{\ell\sigma} \quad (5.3.2.a)$$

and 
$$n_{\ell} = n_{\ell\bar{\sigma}} + n_{\ell\sigma}, \quad (5.3.2.b)$$

so that we can make the approximation

$$\langle\langle m_{\ell\bar{\sigma}} c_{\ell\bar{\sigma}}^{\dagger} c_{k\bar{\sigma}} c_{\ell\sigma}, c_{j\sigma}^{\dagger} \rangle\rangle = \langle m_{\ell\bar{\sigma}} \rangle \cdot \Gamma_{\ell j\sigma}^{\ell k} = m_{\sigma} \cdot \Gamma_{\ell j\sigma}^{\ell k} \quad (5.3.3.a)$$

$$\langle\langle n_{\ell} c_{\ell k\sigma}^{\dagger} c_{\ell\bar{\sigma}} c_{\ell\sigma}, c_{j\sigma}^{\dagger} \rangle\rangle = \langle n_{\ell} \rangle \cdot \Gamma_{\ell j}^{k\ell} = n_{\ell} \cdot \Gamma_{j\ell\sigma}^{k\ell}, \quad (5.3.3.b)$$

which is equivalent to the BM approximation in the limit  $m_{\sigma} = 0$  and  $n = 1$ . This approximation may be considered as the generalization of BM approximation.

Since we have already included other correlation into  $\epsilon_k$  and  $V_{\ell k}$  of the Hamiltonian,  $\Gamma_{kj\sigma}^{\ell k}$  and  $\Gamma_{kj\sigma}^{k\ell}$  can be approximated as being zero, while  $\Gamma_{\ell j\sigma}^{kk'}$  is approximated as follow

$$\Gamma_{\ell j\sigma}^{kk'} = n_{kk'}^{\sigma} \cdot G_{\ell\ell}^{\sigma} \cdot \delta_{\ell j} \quad (5.3.4)$$

Thus 5.3.1.a, b and c become

$$(\omega - \epsilon_k) \cdot \Gamma_{kj\sigma}^{\ell\ell} = \frac{n_{\bar{\sigma}}}{2\pi} \cdot \delta_{kj} + V_{k\ell} \cdot \Gamma_{\ell j\sigma}^{\ell\ell} \quad , \quad (5.3.5.a)$$

$$(\omega - \epsilon_k - U m_{\bar{\sigma}}) \cdot \Gamma_{\ell j\sigma}^{\ell k} = \frac{n_{\bar{\sigma}}}{2\pi} \cdot \delta_{\ell j} + V_{k\ell} \cdot \Gamma_{\ell j\sigma}^{\ell\ell} - (\sum_{k'} V_{k'\ell} \cdot n_{kk'}^{\bar{\sigma}}) \cdot G_{\ell\ell}^{\sigma} \cdot \delta_{\ell j} \quad , \quad (5.3.5.b)$$

$$(\omega - \epsilon_k - 2\epsilon_{\ell} - U n) \cdot \Gamma_{\ell j\sigma}^{k\ell} = \frac{n_k}{2\pi} \cdot \delta_{\ell j} - V_{\ell k} \cdot \Gamma_{\ell j\sigma}^{\ell\ell} + (\sum_{k'} V_{\ell k'} \cdot n_{kk'}^{\bar{\sigma}}) \cdot G_{\ell\ell}^{\sigma} \cdot \delta_{\ell j} \quad (5.3.5.c)$$

Substituting these into 4.5.24.a and b, we have

$$\begin{aligned} (\omega - \epsilon_{\ell} - U) \cdot \Gamma_{\ell j\sigma}^{\ell\ell} &= \frac{n_{\bar{\sigma}}}{2\pi} \cdot \delta_{\ell j} + \frac{1}{2\pi} \cdot \sum_k \left[ V_{\ell k} \cdot \left( \frac{n_{\bar{\sigma}} \cdot \sigma_{kj}}{\omega - \epsilon_k} + \frac{n_{\bar{\sigma}} \cdot \delta_{\ell j}}{\omega - \epsilon_k - U m_{\bar{\sigma}}} \right) - \frac{V_{k\ell} \cdot n_{k\ell}^{\bar{\sigma}} \cdot \delta_{\ell j}}{\omega + \epsilon_k - 2\epsilon_{\ell} - U n} \right] \\ &+ \sum_k |V_{\ell k}|^2 \cdot \left[ \frac{1}{\omega - \epsilon_k} + \frac{1}{\omega - \epsilon_k - U m_{\bar{\sigma}}} + \frac{1}{\omega + \epsilon_k - 2\epsilon_{\ell} - U n} \right] \cdot \Gamma_{\ell j\sigma}^{\ell\ell} + \sum_k \left[ \frac{V_{\ell k} \cdot (\sum_{k'} V_{k'\ell} \cdot n_{kk'}^{\bar{\sigma}})}{\omega - \epsilon_k - U m_{\bar{\sigma}}} \right. \\ &\left. - \frac{V_{k\ell} \cdot (\sum_{k'} V_{\ell k'} \cdot n_{kk'}^{\bar{\sigma}})}{\omega - \epsilon_k - 2\epsilon_{\ell} - U n} \right] \cdot G_{\ell\ell}^{\sigma} \cdot \delta_{\ell j} \quad . \quad (5.3.6) \end{aligned}$$

Defining;

$$\Sigma_A = \Sigma_O + \Sigma_m - \Sigma_n \quad , \quad (5.3.7)$$

$$\text{where } \Sigma_O = \sum_k \frac{|V_{\ell k}|^2}{\omega - \epsilon_k} \quad , \quad \Sigma_m = \sum_k \frac{|V_{\ell k}|^2}{\omega - \epsilon_k - U m_{\bar{\sigma}}} \quad , \quad \Sigma_n = \sum_k \frac{|V_{\ell k}|^2}{\omega + \epsilon_k - 2\epsilon_{\ell} - U n} \quad ; \quad (5.3.8)$$

$$\bar{V}_{k\ell} = \sum_{k'} V_{k'\ell} \cdot n_{kk'}^{\bar{\sigma}} \quad (5.3.9)$$

$$\text{and } \bar{\Sigma}_m = \sum_k \frac{V_{\ell k} \cdot \bar{V}_{k\ell}}{\omega - \epsilon_k - U m_{\bar{\sigma}}} \quad , \quad \bar{\Sigma}_n = \sum_k \frac{\bar{V}_{\ell k} \cdot V_{k\ell}}{\omega + \epsilon_k - 2\epsilon_{\ell} - U n} \quad ; \quad (5.3.10)$$

$$n_{\bar{\sigma}}^{\bar{\sigma}} = \sum_k \frac{V_{\ell k} \cdot n_{\ell k}^{\bar{\sigma}}}{\omega - \epsilon_k - U m_{\bar{\sigma}}} \quad , \quad n_n^{\bar{\sigma}} = \sum_k \frac{V_{k\ell} \cdot n_{k\ell}^{\bar{\sigma}}}{\omega + \epsilon_k - 2\epsilon_{\ell} - U n} \quad , \quad (5.3.11)$$

equation 5.3.6 becomes

$$\begin{aligned}
 (\omega - \epsilon_{\lambda} - U - \Sigma_{\Lambda}) \cdot \Gamma_{\lambda j \sigma}^{\lambda \lambda} = & \frac{1}{2\pi} \cdot \left[ (n_{\sigma} + n_m^{\bar{\sigma}} - n_n^{\bar{\sigma}}) \cdot \delta_{\lambda j} + \sum_k \frac{n_{\sigma} \cdot V_{\lambda k}}{\omega - \epsilon_k} \cdot \delta_{\kappa j} \right] \\
 & + (\bar{\Sigma}_m - \bar{\Sigma}_n) \cdot G_{\lambda \lambda}^{\sigma} \cdot \delta_{\lambda j} .
 \end{aligned} \tag{5.3.12}$$

#### 5.4 The correlation effect in H-chemisorption.

Several authors have studied the correlation effect in impurity and chemisorption problems.<sup>90-98</sup> We will now discuss the relation of three decoupling schemes : the Hubbard decoupling scheme as applied to the impurity problem by Hewson (HH),<sup>90-93</sup> Bell-Madhukar (BM) decoupling scheme which was applied to the microscopic, self-consistent, Hamiltonian by BM<sup>97,98</sup> which we have applied to Anderson Hamiltonian as discussed in 5.3, and Brenig-Schönhammer (BS) self-energy matrix method in weak and strong chemisorbed decoupling scheme.<sup>96</sup> All of these schemes will be discussed under the use of the matrix formalism as proposed in 5.1 and appendix D. The dependence of  $A_{\sigma}$  and  $B_{\sigma}$  on  $V_{\sigma}$  will now be given.

First, we adopt the admixing process, i.e

$$V_{\sigma} = 0_{\sigma},$$

then the two particle Green function can be written independent of the single particle Green function (see 4.5.9), that is

$$B_{\sigma} = 0_{\sigma}.$$

Equation 5.1.7 now becomes

$$G_{\sigma}^0 = g_{\sigma} \cdot (I_{\sigma} + U \cdot A_{\sigma}^0) \cdot \quad (5.4.1)$$

This result is common to all three approximations as the first fundamental Green function which can be calculated exactly without any approximation on Anderson Hamiltonian (or saying that it is exact as Anderson Hamiltonian is exact in the limit of  $V_{\ell k} = 0$ ).

Let us define the number matrix  $N_{\sigma}$  as

$$N_{\sigma} = \begin{bmatrix} n_{11} & n_{12} \\ n_{21} & n_{22} \end{bmatrix}, \quad (5.4.2)$$

where the matrix elements corresponding to the spin  $\sigma$  electron number are

$$(n_{11})_{\ell\ell} = n_{\bar{\sigma}}, \quad (n_{12})_{\ell k} = n_{k\ell}^{\bar{\sigma}}, \quad (n_{21})_{k\ell} = n_{\ell k}^{\bar{\sigma}}, \quad (n_{22})_{kk'} = n_{k'k}^{\bar{\sigma}}.$$

If we define the new isolated single particle matrix  $g'_{\sigma}$  as having the physical meaning of being an electron propagator of spin  $\sigma$  when the isolated atom has an electron of spin  $\bar{\sigma}$  already occupied, and it having the following form

$$g'_{\sigma} = \begin{bmatrix} g'_{11} & 0_{12} \\ 0_{21} & g'_{22} \end{bmatrix}, \quad (5.4.3)$$



where  $g'_{11} = \frac{1/2\pi}{\omega - \epsilon_l - U}$  and  $g'_{22} = g_{22}$  ,

we get  $A_{\sigma}^{\circ} = I_{\sigma} (5) \cdot (2\pi \cdot N_{\sigma}(1) \cdot g'_{\sigma}) = I_{\sigma} (5) \cdot (2\pi \cdot g'_{\sigma} \cdot N_{\sigma}(1)) \cdot (5.4.4)$

The non-hybridized Green function  $G^{\circ}$  is then given as

$$G_{\sigma}^{\circ} = g_{\sigma} + 2\pi \cdot U \cdot g_{\sigma} \cdot I_{\sigma}(5) \cdot N_{\sigma}(1) \cdot g'_{\sigma} \quad (5.4.5)$$

The sub-matrix of  $G_{\sigma}^{\circ}$  are

$$G_{11}^{\circ} = g_{11} + 2\pi \cdot U \cdot g_{11} \cdot n_{11} \cdot g'_{11} , G_{22}^{\circ} = g_{22} , G_{12}^{\circ} = 0_{12} , G_{21}^{\circ} = 0_{21} \cdot (5.4.6)$$

The first equation of 5.4.6 is equivalent to equation 4.5.10

From 4.5.25.a and b, we find that the HH approximation corresponds to matrix expression

$$\Lambda_{\sigma}^{(1)} = A_{\sigma}^{\circ} \quad \text{and} \quad B_{\sigma}^{(1)} = (2\pi)^2 \cdot A_{\sigma}^{\circ} \cdot V_{\sigma} \quad (5.4.7)$$

Substituting this into 5.1.7, we get

$$(I_{\sigma} - 2\pi \cdot g_{\sigma} \cdot (I_{\sigma} + U \cdot \Lambda_{\sigma}^{\circ}) \cdot V_{\sigma}) \cdot G_{\sigma} = g_{\sigma} \cdot (I_{\sigma} + U \cdot \Lambda_{\sigma}^{\circ}) \cdot$$

Using 5.4.5, we can write the above equation as

$$(I_{\sigma} - 2\pi \cdot G_{\sigma}^{\circ} \cdot V_{\sigma}) \cdot G_{\sigma} = G_{\sigma}^{\circ} \quad .$$

We can solve it to get

$$G_{\sigma} = (I_{\sigma} - 2\pi \cdot G_{\sigma}^{\circ} \cdot V_{\sigma})^{-1} \cdot G_{\sigma}^{\circ} \quad . \quad (5.4.8)$$

Since  $G_{\sigma}^{\circ}$  is the type I matrix and  $V_{\sigma}$  is the type II matrix, the matrix  $G_{\sigma}^{\circ} \cdot V_{\sigma}$  is type II matrix (see appendix D). Equation 5.4.8 thus becomes

$$G_{\sigma} = G_{\sigma}^{\circ} + \frac{2\pi \cdot G_{\sigma}^{\circ} \cdot V_{\sigma} \cdot G_{\sigma}^{\circ} + (2\pi)^2 \cdot G_{\sigma}^{\circ} \cdot V_{\sigma} \cdot G_{\sigma}^{\circ} \cdot V_{\sigma} \cdot G_{\sigma}^{\circ}}{1 - \lambda_1}, \quad (5.4.9)$$

where

$$\begin{aligned} \lambda_1 &= (2\pi \cdot G_{\sigma}^{\circ} \cdot V_{\sigma})_{12} (2\pi \cdot G_{\sigma}^{\circ} \cdot V_{\sigma})_{21} \\ &= (2\pi)^2 \cdot G_{11}^{\circ} V_{12} G_{22}^{\circ} V_{21} = (2\pi)^2 \cdot G_{11}^{\circ} V_{12} \epsilon_{22} V_{21}. \end{aligned} \quad (5.4.10)$$

The sub-matrix is given as

$$G_{11} = G_{11}^{\circ} + \frac{(2\pi)^2 \cdot G_{11}^{\circ} V_{12} \epsilon_{22} V_{21} G_{11}^{\circ}}{1 - \lambda_1} = \frac{G_{11}^{\circ}}{1 - \lambda_1}, \quad (5.4.11.a)$$

$$G_{22} = \epsilon_{22} + \frac{(2\pi)^2 \cdot \epsilon_{22} V_{21} G_{11}^{\circ} V_{12} \epsilon_{22}}{1 - \lambda_1}, \quad (5.4.11.b)$$

$$G_{12} = \frac{2\pi \cdot G_{11}^{\circ} V_{12} \epsilon_{22}}{1 - \lambda_1}, \quad (5.4.11.c)$$

$$G_{21} = \frac{2\pi \cdot \epsilon_{22} V_{21} G_{11}^{\circ}}{1 - \lambda_1}, \quad (5.4.11.d)$$

where equation 5.4.11.a equivalent to the equation 4.5.27.a. All single particle Green functions of the HH approximation are obtained.

The second approximation, the BM approximation, has been discussed in some detail for Anderson Hamiltonian in 5.3. From equation 5.3.13, we have

$$A_{\sigma}^{(2)} = 2\pi \cdot I_{\sigma}(5) \cdot \bar{g}_{\sigma} \cdot (N_{\sigma}(1) + V_{\sigma} \cdot g_{\sigma} \cdot N_{\sigma}(1) + V_{\sigma} \cdot g_{m\sigma} \cdot N_{\sigma}(2) - N_{\sigma}(2) \cdot g_{n\sigma} \cdot V_{\sigma}) \quad (5.4.12.a)$$

$$\text{and } B_{\sigma}^{(2)} = (2\pi)^2 \cdot I_{\sigma}(5) \cdot \bar{g}_{\sigma} \cdot (V_{\sigma} \cdot N_{\sigma}(1) \cdot g_{m\sigma} \cdot V_{\sigma} - V_{\sigma} \cdot g_{n\sigma} \cdot N_{\sigma}(1) \cdot V_{\sigma}) \quad (5.4.12.b)$$

where  $\bar{g}_{\sigma}$ ,  $g_{m\sigma}$  and  $g_{n\sigma}$  are the renormalized Green functions define as follows

$$\bar{g}_{\sigma} = \begin{bmatrix} \bar{g}_{11} & 0_{12} \\ 0_{21} & g_{22} \end{bmatrix}, \quad g_{m\sigma} = \begin{bmatrix} g_{m11} & 0_{12} \\ 0_{21} & g_{m22} \end{bmatrix}, \quad g_{n\sigma} = \begin{bmatrix} g_{n11} & 0_{12} \\ 0_{21} & g_{n22} \end{bmatrix} \quad (5.4.13)$$

The matrix elements are

$$(\bar{g}_{11})_{\ell\ell} = \frac{1/2\pi}{\omega - \epsilon_{\ell} - U - \Sigma_{\Lambda}}, \quad (g_{m22})_{kk'} = \frac{\delta_{kk'}/2\pi}{\omega - \epsilon_k - U m_{\sigma}}, \quad (g_{n22})_{kk'} = \frac{\delta_{kk'}/2\pi}{\omega + \epsilon_k - 2\epsilon_{\ell} - U n}$$

while  $(\bar{g}_{22})_{kk'}$ ,  $(g_{m11})_{\ell\ell}$  and  $(g_{n11})_{\ell\ell}$  can be defined arbitrarily

since all matrix in 5.4.12 are projected by  $I_{\sigma}(5)$  such that the terms involving these matrix elements disappeared at the result  $A_{\sigma}^{(2)}$  and  $B_{\sigma}^{(2)}$ . Since the matrix elements of  $B_{\sigma}^{(2)}$  are given that only  $B_{11}$  is not zero, applying this to the equation 5.1.11, we get

$$\lambda_2 = \frac{(2\pi)^2 \cdot g_{11} V_{12} g_{22} V_{21}}{1 - (2\pi) \cdot U \cdot g_{11} B_{11}} \quad (5.4.14)$$

$$\text{Defining } \Sigma_{\text{I}} = 2\pi \cdot V_{12} g_{22} V_{21} + U \cdot B_{11}, \quad (5.4.15)$$

$$f_1^{\bar{\sigma}} = \frac{U \cdot \bar{\epsilon}_{11}^{-1} \Lambda_{11}}{U + \Sigma_A - \Sigma_I} \quad \text{and} \quad f_2^{\bar{\sigma}} \cdot V_{12} \epsilon_{22} = \frac{U \cdot \bar{\epsilon}_{11}^{-1} \Lambda_{12}}{U + \Sigma_A - \Sigma_I} \quad (5.4.16)$$

and from 5.1.14.a, we get

$$G_{11} = \frac{\epsilon_{11}}{1 - 2\pi \cdot \epsilon_{11} \cdot \Sigma_I} + \frac{\epsilon_{11} \cdot U \cdot \bar{\epsilon}_{11}^{-1} \Lambda_{11}}{1 - 2\pi \cdot \epsilon_{11} \cdot \Sigma_I},$$

which can be simplified with the use of the definition 5.4.16 to be

$$G_{11} = \frac{\epsilon_{11}}{1 - 2\pi \cdot \epsilon_{11} \cdot \Sigma_I} \cdot (1 - f_1^{\bar{\sigma}}) + \frac{\epsilon'_{11}}{1 - 2\pi \cdot \epsilon'_{11} \cdot \Sigma_A} \cdot f_1^{\bar{\sigma}} \quad (5.4.17.a)$$

Similarly, from 5.1.14.b, c and d, we have

$$\begin{aligned} G_{22} &= \epsilon_{22} + \frac{(2\pi)^2 \cdot \epsilon_{22} V_{21} \epsilon_{11} \cdot (U \cdot \bar{\epsilon}_{11}^{-1} \Lambda_{12} + V_{12}) \cdot \epsilon_{22}}{1 - 2\pi \cdot \epsilon_{11} \cdot \Sigma_I} \\ &= \epsilon_{22} + (2\pi)^2 \cdot \epsilon_{22} V_{21} \cdot \left[ \frac{\epsilon_{11}}{1 - 2\pi \cdot \epsilon_{11} \cdot \Sigma_I} \cdot (1 - f_2^{\bar{\sigma}}) + \frac{\epsilon'_{11}}{1 - 2\pi \cdot \epsilon'_{11} \cdot \Sigma_A} \cdot f_2^{\bar{\sigma}} \right] \cdot V_{12} \epsilon_{22} \end{aligned} \quad (5.4.17.b)$$

$$G_{12} = \left[ \frac{\epsilon_{11}}{1 - 2\pi \cdot \epsilon_{11} \cdot \Sigma_I} \cdot (1 - f_2^{\bar{\sigma}}) + \frac{\epsilon'_{11}}{1 - 2\pi \cdot \epsilon'_{11} \cdot \Sigma_A} \cdot f_2^{\bar{\sigma}} \right] \cdot V_{12} \epsilon_{22}, \quad (5.4.17.c)$$

$$G_{21} = \epsilon_{22} V_{21} \cdot \left[ \frac{\epsilon_{11}}{1 - 2\pi \cdot \epsilon_{11} \cdot \Sigma_I} \cdot (1 - f_1^{\bar{\sigma}}) + \frac{\epsilon'_{11}}{1 - 2\pi \cdot \epsilon'_{11} \cdot \Sigma_A} \cdot f_1^{\bar{\sigma}} \right]. \quad (5.4.17.d)$$

All single particle Green functions are now solved. The Green functions are now used to determine,

$$n_{ij} = \langle c_i^\dagger c_j \rangle = \lim_{s \rightarrow 0} \int d\omega \cdot F(\omega) \cdot [G_{ji}(\omega + is) - G_{ji}(\omega - is)],$$

where  $G_{ji}$  is shown to be the function of  $n_{rs}$ . This system of equations must be solved self-consistently. We have the system of equation in matrix form

$$N_\sigma = F[N_{\bar{\sigma}}], \quad (5.4.18)$$

and the self-consistent condition is that  $N$  must satisfy

$$N_\sigma = F[N_{\bar{\sigma}}] \quad \text{and} \quad N_{\bar{\sigma}} = F[N_\sigma], \quad (5.4.19.a)$$

$$\text{or} \quad N_\sigma - F[F[N_\sigma]] = 0. \quad (5.4.19.b)$$

This problem is very complicated involving a lot of numerical work. Note that the approximation shows explicitly the meaning of two pole propagators.

The third decoupling scheme is that BS scheme, which is given in appendix E. Unfortunately, this decoupling scheme provides only connection between  $\Gamma_{ll\sigma}^{ll}$  and  $G_{ll}^\sigma$  as shown in E41, but not the connection between  $\Gamma_{lk\sigma}^{ll}$  and  $G_{ll}^\sigma$ . Therefore we can not use the matrix formalism. However, if we work self-consistently only with  $n_{\pm\sigma}$ , we need not to know any other Green function. BS use the self-energy matrix formalism to solve the Green function  $G_{ll}^\sigma$ . From E31 and E37,  $G_{ll}^\sigma$  also shows two pole property.

BM have shown the connection between their result and BS's weak coupling limits, i.e.<sup>98</sup>

$$m(\omega) = \frac{1}{2}(\Sigma_0(\omega) - 2\Sigma_k V_{\beta k} \cdot n_{k\ell}^\sigma) . \quad (5.4.20)$$

We do not believe this to be correct since BS derive  $m(\omega)$  in such a way that it is consistent with  $n_\sigma$  only,<sup>96</sup> while BM treats all  $n_{ij}^\sigma$  self-consistently.<sup>98</sup>

BS have shown that the photoemission spectra can be explained by a two pole Green function.<sup>96</sup> The simplest approximation that has this property is HH approximation. Although BM and its generalized yield a complicate function, the resulting Green function does show the two pole property explicitly. BS approximation produces a Green function which also shows two pole property, however, it is not shown explicitly.

HF, HH, BM and BS approximations, as we have shown, are general and applicable to both magnetic impurity and chemisorption problems.

We have seen that there are many methods which yield the same result that the Green function has two poles when the correlation effect is considered. It is to be interpreted that there exist two propergator, which do not interact with others directly, but do interact with extended electron. In weak coupling limit, the indirect interaction between the propergator is small. Therefore each propergator can independently develope

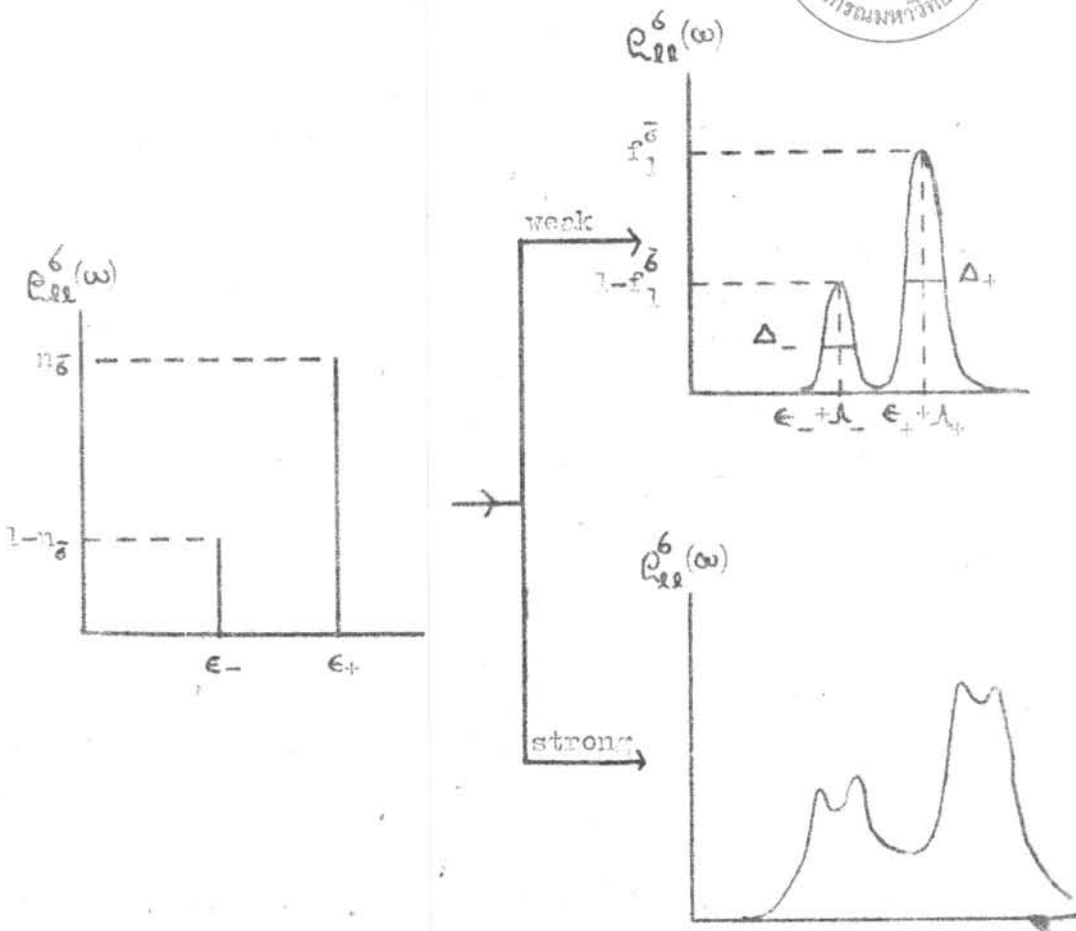


Fig. 5.4.1 : The qualitative change of  $\text{Re} \epsilon^2(\omega)$  with the correlation effect in weak and strong coupling potentials  $V_{Q1}$ .

into a virtual bound state of small width (see Fig 5.4.1.a). This has been shown in generalized BM expression 5.4.18.a. When  $V_{\ell k}$  becomes stronger the generalized BM approximation fails since the indirect interaction is no longer small. In this case BS approximation is better. The splitting of + and - peaks is due to the formation of (classical) chemical bond between the nearest-neighbor metal atoms and the adatom. When  $V_{\ell k}$  is very large the problem can be better treated as  $M_n H$  molecule adsorbed on metal surface.

The BM decoupling has been shown by BM to be correct to order  $V_{\ell k}^2$  in weak coupling limit.<sup>98,100,101</sup> If we generalized the BM scheme more than the previous generalization we have done by keeping only the approximation 5.3.3.a and b, which is equivalent to

$$\langle\langle n_{\ell \pm \sigma} c_{p\bar{\sigma}} c_{q\bar{\sigma}} c_{r\sigma} \rangle\rangle = n_{\pm \sigma} \langle\langle c_{p\bar{\sigma}} c_{q\bar{\sigma}} c_{r\sigma} \rangle\rangle,$$

and applying all two particle Green function in 5.3.1.a, b, c to equations of motion again, we find that the two particle are closed without any additional approximation. All two particle Green function's equation of motion are the following

$$(\omega - \epsilon_{\ell} - U) \cdot \Gamma_{\ell j \sigma}^{\ell \ell} = \frac{n_{\bar{\sigma}}}{2\pi} \cdot \delta_{\ell j} + \sum_k (V_{\ell k} \cdot (\Gamma_{\ell j \sigma}^{\ell k} + \Gamma_{k j \sigma}^{\ell \ell}) - V_{k \ell} \cdot \Gamma_{\ell j \sigma}^{k \ell}) \quad (5.4.21.a)$$

$$(\omega - \epsilon_k) \cdot \Gamma_{k j \sigma}^{\ell \ell} = \frac{n_{\bar{\sigma}}}{2\pi} \cdot \delta_{k j} + V_{k \ell} \cdot \Gamma_{\ell j \sigma}^{\ell \ell} + \sum_{k'} (V_{\ell k'} \cdot \Gamma_{k j \sigma}^{\ell k'} - V_{k \ell} \cdot \Gamma_{k j \sigma}^{k \ell}) \quad (5.4.21.b)$$



$$(\omega - \varepsilon_k - m_\sigma U) \cdot \Gamma_{\ell j \sigma}^{\ell k} = \frac{n_{\ell k}^\sigma}{2\pi} \cdot \delta_{\ell j} + V_{k\ell} \cdot \Gamma_{\ell j \sigma}^{\ell \ell} + \sum_{k'} (V_{\ell k} \cdot \Gamma_{k j \ell}^{\ell k} - V_{k\ell} \cdot \Gamma_{\ell j \sigma}^{k k}), \quad (5.4.21.c)$$

$$(\omega + \varepsilon_k - 2\varepsilon_\ell - nU) \cdot \Gamma_{\ell j \sigma}^{k \ell} = \frac{n_{k \ell}^\sigma}{2\pi} \cdot \delta_{\ell j} - V_{\ell k} \cdot \Gamma_{\ell j \sigma}^{\ell \ell} + \sum_{k'} (V_{\ell k} \cdot (\Gamma_{\ell j \sigma}^{k k} + \Gamma_{k j \sigma}^{k \ell})), \quad (5.4.21.d)$$

$$(\omega + \varepsilon_\ell - \varepsilon_{k'} - \varepsilon_k + n_\sigma U) \cdot \Gamma_{k j \sigma}^{\ell k'} = \frac{n_{\ell k'}^\sigma}{2\pi} \cdot \delta_{k j} + V_{k'\ell} \cdot \Gamma_{k j \sigma}^{\ell \ell} + V_{k\ell} \cdot \Gamma_{\ell j \sigma}^{\ell k'} - \sum_{k''} V_{k''\ell} \cdot \Gamma_{k j \sigma}^{k'' k}, \quad (5.4.22.a)$$

$$(\omega + \varepsilon_{k''} - \varepsilon_\ell - \varepsilon_k - n_\sigma U) \cdot \Gamma_{k j \sigma}^{k'' \ell} = \frac{n_{k'' \ell}^\sigma}{2\pi} \cdot \delta_{k j} - V_{\ell k''} \cdot \Gamma_{k j \sigma}^{\ell \ell} + V_{k\ell} \cdot \Gamma_{\ell j \sigma}^{k'' \ell} + \sum_{k'} V_{\ell k'} \cdot \Gamma_{k j \sigma}^{k'' k'}, \quad (5.4.22.b)$$

$$(\omega + \varepsilon_{k''} - \varepsilon_{k'} - \varepsilon_k - n_\sigma U) \cdot \Gamma_{\ell j \sigma}^{k'' k'} = \frac{n_{k'' k'}^\sigma}{2\pi} \cdot \delta_{\ell j} - V_{\ell k''} \cdot \Gamma_{\ell j \sigma}^{\ell k'} + V_{k'\ell} \cdot \Gamma_{\ell j \sigma}^{k'' \ell} + \sum_{k} V_{\ell k} \cdot \Gamma_{k j \sigma}^{k'' k'}, \quad (5.4.22.c)$$

$$(\omega + \varepsilon_{k''} - \varepsilon_{k'} - \varepsilon_k) \cdot \Gamma_{k k \sigma}^{k'' k'} = \frac{n_{k'' k'}^\sigma}{2\pi} \cdot \delta_{k j} - V_{\ell k''} \cdot \Gamma_{k j \sigma}^{\ell k'} + V_{k'\ell} \cdot \Gamma_{k j \sigma}^{k'' \ell} + V_{k\ell} \cdot \Gamma_{\ell j \sigma}^{k'' k'}. \quad (5.4.22.d)$$

Since rank and order of this system of equations are equal, there exist an unique set of solutions. Thus the two particle Green function can be written explicitly independent of the single particle Green function, or  $B$  is zero matrix.