CHAPTER I

INTRODUCTION.

In this century, solid catalysis has advanced from a labolatory curiousity. to become a major component of the chemical and petroleum industries. The use of catalysts was initially a mysterious art requiring laborious empirical testing. Solid catalysts work by adsorbing at least one reactant. Thus, a knowledge of adsorption is necessary for a fundamental understanding of catalysis.[1,2]

The adsorption phenomenon is a fundamental not only to solid catalysts, but also crystal growth, corrosion, surface reaction etc., the mysterious part of modern chemistry. This is the sad story, since all those mysterious chemistry are basic to the technology nowadays.

Adsorption on solid surface is a complex phenomenon, involving higher density of mobile phase, which may be liquids or gases, near the surface. Also the solid surface are not uniform. They consist of sites with a broad distribution of adsorption energy and irregular surface patterns. The adsorbed molecules may be mobile or immobile. They may be independent of each other or they may interact with their nearest neighbours or even more distant ones and as a result, undergo phase transformations.[2,3]

The solid surface itself is a vaguely understood part of solid state physics today.[4-8]   In the usual solid state physics description, the solid is considered to be infinitely large, so that the effect of surface is cancelled out. Furthermore the surface properties are difficult to measure since the clean surface, which was impossible until Langmuir (1909) discovered UHV (Ultra High Vacuum) techniques,[9] are required. After the discovery of the UHV techniques, the experiment on the surface phenomena progress very fast.[1,8]

1.1 Adsorption[2,3,10]

Since the adsorption process is spontaneous, the free energy G (Gibbs free energy) of the system decreases. The thermodynamics relation of the free energy change is

$$\Delta G = \Delta H - T \cdot \Delta S .$$ (1.1.1)

Furthermore, because the molecules of the mobile phase must lose some degree of translational freedom, there is a decrease of entropy S and hence the enthalpy H decrease, i.e. the adsorption is exothermic. This does not necessary   to happen   since in dissociative adsorption the entropy may increase, and it is possible for enthalpy to increase. When this occurs the adsorption is endothermic.

The adsorption may also be classified in other ways. It may be classified as being physical or chemical, where the distinction is based on the magnitude of the heat of adsorption.

Although widely used, this classification is not very precise. It can also be classified as being monolayer or multilayer. Here again, the distinction is not very exact because the building of multilayer often begins before the first layer is complete. It can also be classified as being localized or nonlocalized. In localized adsorption, molecules are considered to be adsorbed at discrete sites, where they reside in position of minimum potential energy.

1.2 Physisorption v.s. chemisorption.[2,3,10,11]

These two technical terms correspond to physical and chemical adsorption. Chemisorption is defined as the adsorption of atoms or molecules on solid surfaces with binding energy in excess of 0.5 eV and involves electron transfer or sharing as distinct from physisorption, which result mainly from dispersion forces. The distinction becomes hazy in borderline cases. In most cases of chemisorption E_b = 1-5 eV.

It was previously thought that the rate of adsorption could be used as a further criterion; i.e. physisorption on plan surface is extremely rapid. However, for porous adsorbents such as charcoal the rate is determined by the rate of diffusion (either through the pores or along the surface), which is not very fast. On the other hand, chemisorption was considered to be an activation process. Although this is true in most cures, it is now accepted that the activation energy for chemisorption of e.g. hydrogen or oxygen on most transition metals may approach zero.

1.3 The scope of the thesis

This thesis is limited to the theoretical study of
the problem of hydrogen chemisorption on solid surface, especially
transition metals and their alloys surface. There are two reasons
for doing this. The first is that nearly all catalysts are
transition metals or their alloys. Another reason is that
hydrogen molecule dissociate into atomic hydrogen when the
chemisorption occur, and the atomic hydrogen description is
theoretically simple and well known.

We shall be interested in the force , involved in
chemisorption, which were first called the residue force by
Langmuir.[9] The semi-empirical approaches will be discussed in
2.1. Recent developments will be briefly reviewed in 2.2. The
most interest model of chemisorption, the Newns-Anderson model,
will be discussed in detail in 2.3. This model forms the basis
of this thesis.

In chapter III we will discuss the metal surface within
the layer concept. This concept is discussed for semi-infinite
crystal model. The tight-binding method is developed for this
model with the layer concept as its shadow in 3.1. We will limit
our discussion to simple cubic lattice in 3.2. The layer secular
equation is shown and solved for small surface perturbation. This
case will be shown to have small phase shift, which is bounded
and trend to be zero as surface perturbation become zero. We then
relate the layer matrix element to the atomic matrix representation,
assuming simple non-degenerated atomic orbitals. The result is

then applied to the calculation of the dispersion part of the self-energy Σ_o in appendix F. The limiting case of the 3-D is shown to give the same result as Newns' semi-elliptic form for 1-D. We also show that instead of finding the local density of states of semi-infinite crystal we can use the bulk(the infinite crystal) local density of states. The Koster-Slater method of finding the bulk density of states is rederived in 3.3. The density of states is given in the integral 3.3.8. This result is further simplified in appendix C.

The theory of localized states in metals is reviewed and discussed in chapter IV. This theory is important for the chemisorption theory because we can formulate this as surface impurity problem. Friedel's virtual states and its further development are discussed in 4.1, 4.2 and 4.3. The phenomenological Hamiltonian or Anderson Hamiltonian is discussed in 4.4. In 4.5 we show in detail that the double-time Green function technique can be use to solve the problem. Hartree-Fock and Hubbard-Hewson approximation are discussed, and the solution are then expressed in the form of Dyson equation. The density distribution of localized states and the self-consistency condition for both approximation are shown in 4.6 and 4.7.

In chapter V the correlation effect is discussed. The double-time Green function's equation of motion are solved by linear algebraic techniques. The matrix formalism introduced in appendix D is used to solve the equation of motion of

single-particle Green function in 5.1. In 5.2 we approximate
the result by using the Hartree Fock approximation. We also
discuss the physical meaning of H-chemisorption within the
Hartree-Fock approximation in this   section. The well known
Bell-Madhukar decoupling scheme is generalized and applied
to Anderson Hamiltonian in 5.3. The Hubbard-Hewson, Bell-Madhukar
and Brenig-Schonhammer (this approximation is worked out in detail
in appendix E) are discussed using the matrix formalism. The
correlation effect and the resulting single-particle Green
function are compared.

In chapter VI, we discuss the inter-relation between
the different results of the previous chapters.

In appendix A, a review of Zubarev double-time Green
function is given. In appendix B, the analytical integration
of electron number n_σ is performed within the Hartree-Fock
approximation. This integration uses the semi-elliptic form
of Δ_0 . In appendix C, the density of states 3.3.8 is shown to
reduce to a simplier form. In appendix D, the block form and
matrix formalism for the single localized state in extended
states are formulated. In appendix E, the mathematical evaluation
of Brenig - Schönhammer scheme   is presented in detail. In
appendix F, we analyse the Δ_0 using the results of chapter
III. We also show the 1-D limit of Δ_0 in this appendix. The
simple numerical scheme of Δ_0 is shown in appendix G.