

## Composite Anderson–Newns model and chemisorption characteristics of nickel-hydrogen system

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**Abstract.** The composite Anderson–Newns model and triangular weighted density of states are used to study the electron density of states, magnetic moment and charge transfer of adatoms for a chemisorbed system. The model has been applied to hydrogen chemisorbed on nickel. It has been observed that with the increase in coverage, number of B–AB states as well as bond strength increases, whereas the magnetic moment and adatom charge decrease with coverage. These results match with the experimental data.

**Keywords.** Chemisorption; density of states; coverage; charge transfer; magnetic moment.

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### 1. Introduction

Chemisorption of gases on the surface of metals, one of the most interesting problems in solid state physics, has helped us understand various processes that take place on the surfaces of metals, viz. corrosion, hydrolysis and catalysis. At present, there are a number of competing theories for chemisorption based on semi-empirical model Hamiltonian or first principle *ab initio* method. Considerable progress has been made in *ab initio* calculations using density functional theory and its local approximation, cluster calculations or coherent potential approximation. Though these methods allow us to carry out high precision calculations of space distribution of electric charge, binding energy, work function changes and other experimental characteristics of an adsorbate-adsorbent system, there are many difficulties when many body effects and correlations in electronic and ionic component of adsorbate are considered.

On the other hand the model Hamiltonian method appears well suited for understanding the experimentally observed features. This is due to the relatively simple microscopic picture of the system used and the possibility of including correlation effects and additional interactions in the adsorbed system by using suitable approximations [1, 2]. Furthermore, equation of motion method can be very useful while including the correlation effects [1]. The first most successful Hamiltonian method proposed by Newns [3] was further improved by many workers [4]. They used Anderson model Hamiltonian for magnetic alloys, to treat the chemisorbed atom as an impurity on the surface, and then solved the problem within the self-consistent Hartree–Fock scheme. A more generalized version of Anderson–Newns model, called the composite Anderson–Ising Model, was proposed by Gavrilenko [5] wherein an attempt was made to incorporate the Coulomb correlations and interactions in the adsorbed system. This model was applied to the case of stochastic arrangement of adatoms on metal surfaces by Gavrilenko *et al* [6] and it was shown that Anderson

criteria for impurity magnetism in metals holds for this type of phase transition also. Later, using this model, characteristics of chemisorption were further investigated by Cardena [2]. The calculations were carried out within the framework of Hartree–Fock approximation for electronic component of adsorbate using Bragg–Williams approximation for ionic component. This theoretical study started showing results of density of states (DOS) which were quite close to that obtained from the angular photoemission spectra [7]. However, no systematic attempt has been made so far to analyse the magnetic and non-magnetic case associated with the chemisorption as a function of the coverage using the triangular weighted density of states (WDOS) for nickel-hydrogen system. The triangular WDOS is a better choice as suggested by Kalkestein and Soven as it provides a better fit compared to the semi-elliptical WDOS [8].

We have studied here the changes in electronic DOS, magnetic moment and charge transfer on chemisorption of hydrogen on a transition metal (nickel) using the composite Anderson-Newns model [5] and the triangular WDOS. We solve this model self consistently within the Hartree–Fock scheme.

In § 2 the general formalism and its assumptions are discussed and a basic expression for the DOS, magnetic moment, charge transfer and chemisorption energy is derived. In § 3 the results obtained by numerical analysis are discussed.

## 2. Basic equations and formalism

Consider a system of  $N_A$  adsorbed hydrogen-like atoms (adatoms) distributed over  $N$ -active centres (adsorption centres) on the metal surface (substrate).  $N_A \leq N$ . Each atom has a rigid bond with the substrate. The configuration of the adatom arrangement over the adsorption centres is not fixed. In the simplest case, Hamiltonian of this system can be written in the form:

$$H = \sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{\alpha} N_{\alpha} \left[ \sum_{\sigma} E n_{\alpha\sigma} + U n_{\alpha\uparrow} n_{\alpha\downarrow} + \sum_{k,\sigma} (V_{ak} b_{\alpha\sigma}^{\dagger} a_{k\sigma} + \text{h.c.}) \right]. \quad (1)$$

Here, sum over  $\alpha$  in (1) is over all adsorption centres, the operator  $N_{\alpha} = C_{\alpha}^{\dagger} C_{\alpha}$  has eigen values 0 or 1.  $C_{\alpha}^{\dagger}$  and  $C_{\alpha}$  are the Fermi amplitude of creation and annihilation operators of adsorption centre,  $\alpha$ ,  $\varepsilon_k$  is the energy spectrum of clean substrate,  $E$  is the ionization potential of adatom.  $n_{k\sigma} = a_{k\sigma}^{\dagger} a_{k\sigma}$ ,  $n_{\alpha\sigma} = b_{\alpha\sigma}^{\dagger} b_{\alpha\sigma}$ , where  $a_{k\sigma}$ ,  $b_{\alpha\sigma}$  are the electron variables for substrate electron and atoms, respectively,  $U$  describes the coulomb interaction of atomic electrons and h.c. means hermitian conjugate.

Here, the difference from the usual form is due to the hopping interactions being proportional to  $V_{ak}(V_{k\alpha})$  which takes into account the indirect interactions between the adatoms. Although this model is linear with respect to ion operator  $N_{\alpha}$  it is not equivalent to ideal lattice model due to these interactions and hence Bethe's approximation cannot be used here. To solve this model, only one localized impurity atom is taken. Then  $N_{\alpha} = 1$  if  $\alpha = A$  and  $N_{\alpha} = 0$  if  $\alpha \neq A$ , and using unrestricted Hartree–Fock approximation (which considers the averaged interactions of all adatoms and substrate) the Hamiltonian reduces to the form which can be easily solved [9]. The electronic properties of the system are described by correlators of type  $\langle n_{\alpha\sigma} \rangle$ ,  $\langle N_{\alpha} n_{\alpha\sigma} \rangle$ ,  $\langle N_{\alpha} b_{\alpha\sigma}^{\dagger} a_{k\sigma} \rangle$ , ..., whereas ionic properties are described by correlators of Ising type  $\langle N_{\alpha} \rangle$ ,  $\langle N_{\alpha} N_{\beta} \rangle$ , ...,  $\langle N_{\alpha} N_{\beta} \dots N_{\delta} \rangle$ , ...

To derive all the related electronic properties of system double time Green's functions are used which are derived by equation of motion method [9]. To derive

electronic properties of the system in the final form Bragg-Williams approximation is used which assumes the distribution of the spin as random and considers the interactions only between nearest neighbours. The important feature of this composite model is that it takes care of both the cases and also the intermediate values of coverage. Finally, the density of states (DOS) of this system can be written as [6]:

$$D(\omega) = \sum_{\sigma} D_{\sigma}(\omega) = \left(\frac{1}{\theta}\right) \text{Im} \ll N_{\alpha} b_{\alpha\sigma}; b_{\alpha\sigma}^{\dagger} \gg_{\omega - i\theta}.$$

Using the assumptions, we get

$$D_{\sigma}(\omega) = \frac{1}{\theta} \left(\frac{a}{2\pi}\right)^d \text{Im} \int \frac{d\omega}{(\omega - E_{\sigma} + \varepsilon_F - (1 - \theta)L(\omega) - \theta P_q(\omega))_{\omega - i\theta}}. \quad (2)$$

The magnetic moment ( $m$ ) measured in units of Bohr magneton and electric charge ( $q$ ) measured in units of electron charge are given by:

$$m = \langle n_{\alpha\uparrow} \rangle - \langle n_{\alpha\downarrow} \rangle, \quad q = 1 - \langle n_{\alpha\uparrow} \rangle - \langle n_{\alpha\downarrow} \rangle,$$

and

$$n_{\alpha} = \int d\omega D_{\sigma}(\omega - \varepsilon_F). \quad (3)$$

By definition, the chemisorption energy  $\Delta E$  is

$$\Delta E = \frac{1}{N_A} \left( \langle H \rangle - \sum_{K,\sigma}^{\text{occ.}} \varepsilon_K \right) - E, \quad (4)$$

where  $H$  is the Hamiltonian of the system and summation is carried over all occupied states of unperturbed system. We have considered a one dimensional model of periodically arranged atoms with lattice constant  $a = 1$  interacting only with its nearest neighbours and taking periodic boundary conditions. Here we have taken energy spectrum,  $\varepsilon_K = \Gamma \cos(K)$  with respect to the centre of the band. One chemisorption centre per site has also been considered. For this case eq. (2) after some simplifications can be written as:

$$D_{\sigma}(\omega) = \frac{1}{\pi} \left(\frac{a}{2\pi}\right) \int_{-\pi/a}^{\pi/a} \frac{(1 - \theta) \Delta(\omega) dq}{\left\{ \left[ \omega - E_{\sigma} + \varepsilon_F - (1 - \theta)\gamma(\omega) - \left(\frac{\theta \beta^2}{\omega - \varepsilon_q + \varepsilon_F}\right) \right]^2 + (1 - \theta)^2 \Delta(\omega)^2 \right\}}, \quad (5)$$

where  $\gamma(\omega) + i\Delta(\omega) = L(\omega - i\theta)$ ,  $\Delta(\omega) = \pi\beta^2 \bar{\rho}(\omega + \varepsilon_F)$  is the weighted DOS states and  $\gamma(\omega)$  is the Hilbert transform of  $\Delta(\omega)$ -function and is given by:

$$\gamma(\omega) = \int \frac{\Delta(\omega) dy}{(\omega - y)}, \quad \text{where } -\pi \leq \text{arc } tg \leq \pi.$$

The corresponding equation for  $\varepsilon_F$  is

$$\frac{1}{N_A} \int_{\varepsilon_F^0}^{\varepsilon_F} d\omega \rho_0(\omega) = \frac{\theta}{\pi} \left( \frac{a}{2\pi} \right) \sum_{\sigma} \int_{-\pi/a}^{\pi/a} dq \times \arctg \left( \frac{(1-\theta)\bar{\Delta}(\varepsilon_F)}{\varepsilon_F - E_{\sigma} - (1-\theta)\bar{\gamma}(\varepsilon_F) - (\theta\beta^2/(\varepsilon_F - \varepsilon_q))} \right) + \theta. \quad (6)$$

The functions  $\Delta(\omega)$  and  $\gamma(\omega)$  are called chemisorption functions, the latter being Hilbert transform of the former. These are related to each other through  $G_{\alpha,\sigma}(\omega) = \gamma(\omega) + i\Delta(\omega)$ . Here, we take the WDOS to be triangular, a more realistic WDOS, as it reveals the salient features of DOS, e.g. the emergence of split off states at very low coverage [9]. The triangular WDOS is given by

$$\Delta(\omega) = \text{Im}[G(\omega)] = \beta^2 [1 - |\omega|] \text{ for } |\omega| < 1 \quad \text{and} \\ = 0 \text{ for } |\omega| > 1. \quad (7)$$

The Hilbert transform of  $\Delta(\omega)$  is

$$\gamma(\omega) = \text{Re}[G_{\alpha,\sigma}(\omega)] = \beta^2/\pi \left[ \ln \left| \frac{1-\omega}{1+\omega} \right| + \omega \ln \left| \frac{(1-\omega)(1+\omega)}{\omega^2} \right| \right], \quad (8)$$

where  $\beta$  is the hybridization parameter, the matrix element of  $V_{\alpha\beta}$ . This is a measure of the adatom-substrate interaction [2] and the behaviour of a typical system depends on the allowed value of this parameter for a given value of  $U$ .

### 3. Numerical results and discussion

The calculation of electronic DOS, magnetic moment and charge transfer for different coverages has been carried out for both magnetic and non-magnetic cases, using triangular WDOS. In order to calculate these values the basic parameters are: ionization level ( $E$ ), the electron affinity level ( $E + U$ ), where  $U$  is the coulomb's interaction between electrons on impurity level,  $\varepsilon_F^0$ , the Fermi level,  $\beta$ , the hybridisation parameter and  $2\Gamma = (\varepsilon_1 - \varepsilon_0)$  the band width of the unperturbed system where  $\varepsilon_1, \varepsilon_0$  are the upper and lower edges of band respectively. There are three situations corresponding to different positions of ionization and affinity level w.r.t. Fermi level parameterised by  $\eta = E - \varepsilon_F + U/2$ . We shall concentrate on the case  $\eta = 0$  corresponding to symmetric Anderson's model.  $n_x$  and  $\varepsilon_F$  are calculated self-consistently using (3), (5) and (6) and all the experimental parameters for nickel are taken ( $E = -4.789$ ,  $U = 6.789$  and  $\varepsilon_F = 0.926$ ) from Newns [3]. The value of adatom integral equals 12.9 eV, as it stands for an isolated hydrogen atom. The determination of this quantity in the presence of substrate surface is extremely difficult, therefore we can safely take it to be 12.9 eV, and compare our results with that of others. All energies are measured in terms of half band width ( $\Gamma$ ) and the position of energy levels w.r.t. substrate band centre. Also  $\varepsilon_F^0 = 0$ .

If  $U/\beta$  is large ( $\approx 20$ ), we have the magnetic case and if  $U/\beta$  is small ( $\approx 8$ ), the non-magnetic. Figures 1 and 2 give the salient features of the electronic DOS vs  $\omega$ , for different coverages, for both magnetic and non-magnetic cases respectively.

Some of the common features for both the cases, are (a) At zero coverage there is only one peak, which is quite consistent with the work of Gavrilenko [6]. Of course, it is

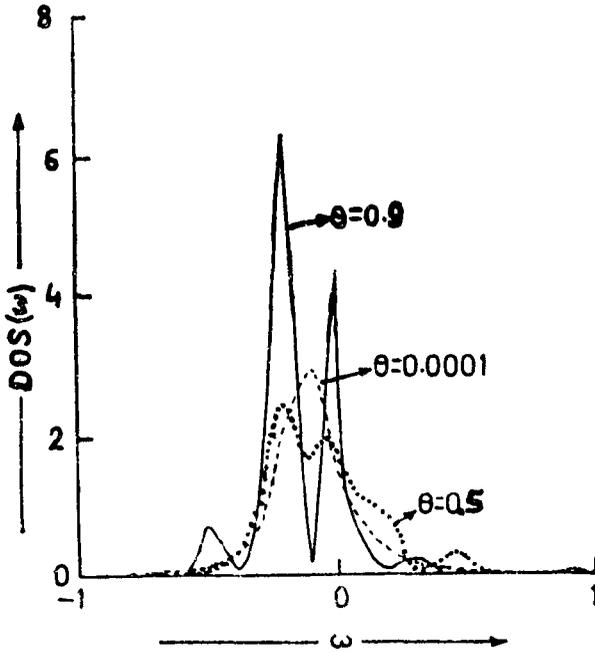


Figure 1. DOS vs  $\omega$  for different coverages  $\theta = 0.0001, 0.5$  and  $0.9$ , for coverage stimulated magnetic case.

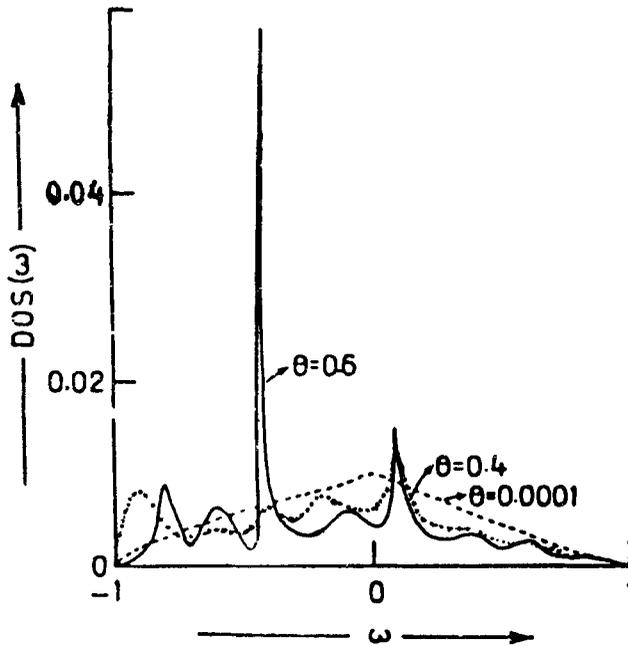


Figure 2. DOS vs  $\omega$  for different coverages  $\theta = 0.0001, 0.4$  and  $0.6$ , for coverage stimulated non-magnetic case.

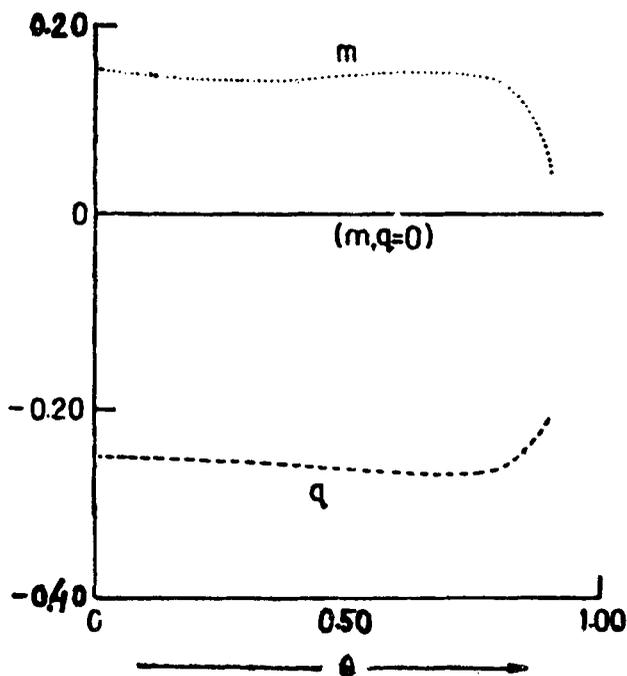


Figure 3. Magnetic moment ( $m$ ) and charge transfer ( $q$ ) vs coverage ( $\theta$ ), for both magnetic and non-magnetic cases.

apparently sensitive to the choice of parameters, particularly  $\beta$ . (b) With increase in coverage ( $\theta$ ), the height of B-AB peaks increases, which implies an increase in the number of B-AB states. This is also in agreement with the findings of Brenig and schonhammer [11] and Gavrilenko [6]. (c) In both the cases, the distance between the B-AB peaks as well as the depth between the peaks increases with increase in coverage ( $\theta$ ), implying increase in bond strength with coverage. This feature for non-magnetic case is in agreement with other approaches and that of Gavrilenko [6]. Whereas if we take  $\beta \approx 1$  in the WDOS, as given by Schrieffer [10], then the behaviour of DOS in this case of nickel-hydrogen system is similar to that discussed here [9]. Thus we conclude that behaviour of DOS is most sensitive to the parameter ( $\beta$ ), which takes into account the interaction between adatom and substrate and its value for each system should be determined separately. (d) In both the cases, at high coverage, the number of B-AB peaks also increases which is due to the correlation effects as pointed out by Brenig and Schonhammer [11]. (e) Further, the characteristic features are (i) Comparison of figures 1 and 2 shows that in the magnetic case, the height of B-AB peaks is higher than that in the non-magnetic case, implying, more number of B-AB states in the magnetic case, as expected. (ii) In the magnetic case, there is a considerable decrease in the magnetic moment at large coverages, [figure 3 (upper curve  $m$ )], which agrees with the results of density functional approach [12]. The charge transfer to the adatoms remains almost constant up to certain  $\theta$  and then starts falling off at large  $\theta$  ( $\approx 0.9$ ), showing neutralization of adatoms, [figure 3 (lower curve  $q$ )]. This is found consistent with the experimental situation [13], whereas, in the non-magnetic case both magnetic moment and charge transfer are zero for all the coverages, [figure 3 (curve  $m, q = 0$ )], as was also mentioned by Gavrilenko [6].

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