

## Cluster Bethe lattice model studies of chemisorption: H on Ni surface

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**Abstract.** The tight binding cluster Bethe lattice model formulated earlier for treating chemisorption systems has been used to study a specific system, namely, hydrogen chemisorption on Ni(100) surface. The hydrogen atom occupies the centre hollow position in agreement with the experimental results.

**Keywords.** Cluster Bethe lattice; chemisorption; Green's functions; transfer functions; hopping integral.

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### 1. Introduction

In an earlier work the present author (Khanra 1983) approximated the surface Green's functions by the tight binding cluster Bethe lattice model (TBCBLM) (Joannopoulos and Yndurain 1974). It was found that for chemisorption of a single-orbital adatom on a single-band tight binding simple cubic solid the model yielded results in excellent agreement with those of Einstein and Schrieffer (1973). Especially, for energy calculations where the detailed structures in the density of states are not very important, but the general shape of the density of states curve is important, this model is quite effective and computationally much simpler than the other tight binding models (Haydock *et al* 1972, 1975; Cyrot-Lackman *et al* 1974). This paper applies the model developed earlier (Khanra 1983) to a specific system. For simplicity we choose the system of hydrogen chemisorption of Ni(100) surface. Section 2 gives the TBCBLM theory, the results of which are given and discussed in §3.

### 2. TBCBLM theory

The TBCBLM is based on the following assumptions (Khanra 1983): (a) There is only one type of orbital on the substrate atoms. For the system considered, this assumption is quite logical since it is well known that the valence structure of transition metals consists of relatively tightly bound *d* bands hybridising with nearby free-electron *s-p* bands. Most of the physical and chemical properties of transition metals are primarily governed by the *d* electrons. For example, bonding properties like the cohesive energy of the transition metals and the heat of formation of transition metal alloys is explained by *d-d* metallic bonds. So, it is natural that in the chemisorption process also the *d* orbitals play the most important role. (b) The correlation effects are not explicitly considered, but can be indirectly considered by modification of the parameter like

adatom energy level etc. (c) The distance between the adatom and the nearest substrate atom is assumed to be the same for chemisorption on top position (A), bridge position (B) and centre position (C).

Now, let us consider a tight binding Hamiltonian

$$H = \sum_i \varepsilon_i |i\rangle \langle i| + \sum_{\substack{ij \\ i \neq j}} V_{ij} |i\rangle \langle j|. \quad (1)$$

We can calculate the Green's functions at any site in the semi-infinite solid from the equation (Joannopoulos and Yndurain 1974)

$$E \langle i|G|j\rangle = \delta_{ij} + \sum_n \langle i|H|n\rangle \langle n|G|j\rangle. \quad (2)$$

where  $\varepsilon_i$  and  $V_{ij}$  in (1) represent the  $i$ th site energy and the hopping interaction between the  $i$ th and the  $j$ th site respectively.  $n$  in (2) is an intermediate site between the  $i$ th and the  $j$ th site. Let us consider a cluster of surface atoms as shown in figure 1. Using (2) the Green's function for an orbital at the 0th site may be written as

$$(E - \varepsilon_m) G_{00}^{SS} = 1 + Z_0 V G_{10}^{SS} + Z_1 V G_{10}^{BS}, \quad (3)$$

where  $\varepsilon_m$  is the energy of the substrate metal atom orbital and  $V$  is the interaction energy between two nearest neighbour (NN) metal atoms.  $Z_0$  and  $Z_1$  are the number of NN's of a surface atom in the same plane and in the adjacent plane respectively. The superscripts *SS* and *BS* indicate that the electron moves on the surface ( $S \leftarrow S$ ) and from surface to bulk ( $B \leftarrow S$ ) respectively. To solve (3) for  $G_{00}^{SS}$  in a closed form we have to solve the following set of equations self-consistently:

$$(E - \varepsilon_m) G_{10}^{SS} = V G_{00}^{SS} + (Z_0 - 1) V G_{20}^{SS} + Z_1 V G_{20}^{BS}, \quad (4)$$

$$(E - \varepsilon_m) G_{10}^{BS} = V G_{00}^{SS} + (Z_1 - 1) V G_{20}^{SB} + (Z_0 + Z_1) V G_{20}^{BB}, \quad (5)$$

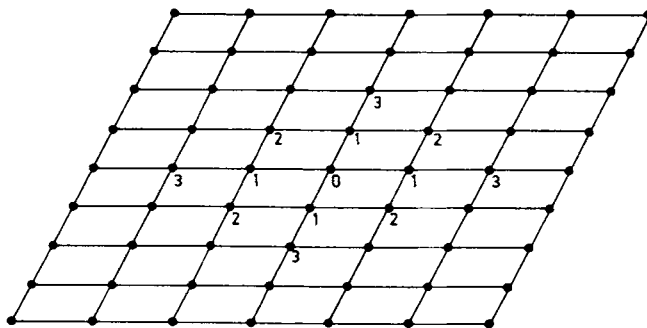
$$(E - \varepsilon_m) G_{20}^{SB} = V G_{10}^{BS} + Z_0 V G_{30}^{SS} + (Z_1 - 1) V G_{30}^{BS}, \quad (6)$$

$$(E - \varepsilon_m) G_{20}^{BB} = V G_{10}^{BS} + (Z_0 + 2Z_1 - 1) V G_{30}^{BB}. \quad (7)$$

Introducing the transfer functions

$$\alpha = G_{n0}^{SS}/G_{n'0}^{SS} = G_{n0}^{SS}/G_{n'0}^{SB}; \quad \beta = G_{n0}^{BS}/G_{n'0}^{SS} = G_{n0}^{BS}/G_{n'0}^{SB};$$

$$\beta' = G_{n0}^{SB}/G_{n'0}^{BS}; \quad \gamma = G_{n0}^{BB}/G_{n'0}^{BB} = G_{n0}^{BB}/G_{n'0}^{BS}. \quad (8)$$



**Figure 1.** Schematic diagram of a surface cluster consisting of a central atom, its 1st, 2nd and 3rd nearest neighbours.

where  $n' = n - 1$ , the equations (4)–(7) reduce to

$$(E - \varepsilon_m) \alpha = V + (Z_0 - 1) V \alpha^2 + Z_1 V \beta \alpha, \tag{4a}$$

$$(E - \varepsilon_m) \beta = V + (Z_1 - 1) V \beta' \beta + (Z_0 + Z_1) \gamma \beta, \tag{5a}$$

$$(E - \varepsilon_m) \beta' = V + Z_0 V \alpha \beta' + (Z_1 - 1) V \beta' \beta, \tag{6a}$$

$$(E - \varepsilon_m) \gamma = V + (Z_0 + 2Z_1 - 1) V \gamma^2. \tag{7a}$$

These transfer functions signify the propagation of an electron from a surface site to another surface site ( $\alpha$ ), from a surface site to a bulk site ( $\beta$ ), from a bulk site to a surface site ( $\beta'$ ) and from a bulk site to another bulk site ( $\gamma$ ). These TF's have to be determined self-consistently.

In the presence of a chemisorbed atom  $\alpha$  will be drastically modified near the adsorbate. Assuming that the other transfer functions are not drastically modified, we can introduce three new surface-surface transfer functions (see figure 2) which satisfy the following set of equations:

$$(E - \varepsilon_m) = 1/G_{00}^{SS} + Z_0 V \alpha_0 + Z_1 V \beta, \tag{9}$$

$$(E - \varepsilon_m) \alpha_0 = V + V \alpha_0 \alpha' + (Z_0 - 2) V \alpha_0 \alpha'' + Z_1 V \alpha_0 \beta, \tag{10}$$

$$(E - \varepsilon_m) \alpha' = (Z_0 - 2) V + (Z_0 - 2) V \alpha \alpha' + Z_1 V \beta \alpha', \tag{11}$$

$$(E - \varepsilon_m) \alpha'' = V + (Z_0 - 3) V \alpha \alpha'' + Z_1 V \beta \alpha''. \tag{12}$$

To treat the chemisorption problem one has to first solve (4)–(7) and then (10)–(12) to calculate the surface Green's function from (9). For chemisorption on top position we have

$$G_{00}^{SS}(A) = 1/(E - \varepsilon_m - Z_0 V \alpha_0 - Z_1 V \beta), \tag{9a}$$

while for chemisorption on bridge and centre position one can write (Einstein and Schrieffer 1973)

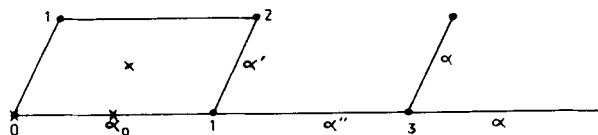
$$G_{00}^{SS}(B) = G_{00}^{SS}(A) + G_{10}^{SS}(A), \tag{13}$$

and  $G_{00}^{SS}(C) = G_{00}^{SS}(A) + 2G_{10}^{SS}(A) + G_{20}^{SS}(A), \tag{14}$

respectively ( $A, B$ , and  $C$  in parentheses of Green's functions indicate the chemisorption sites). The chemisorption energy  $E_c$  is then given by (Einstein and Schrieffer 1973)

$$E_c = 2(E_s - E_0) - \frac{2}{\pi} \int_{E_0}^{E_F} \text{Im} \ln \left( 1 - \frac{V_1^2 G_{00}^{SS}(X)}{E - \varepsilon_a - i\delta} \right) dE, \tag{15}$$

where  $E_s, E_0, E_F$  and  $\varepsilon_a$  are the energies corresponding to the split-off states below the band, the lower band edge, the Fermi level and the adatom level respectively.  $V_1$  is the metal atom-adsorbate interaction.  $X$  may be  $A$  or  $B$  or  $C$  depending on the site of chemisorption.



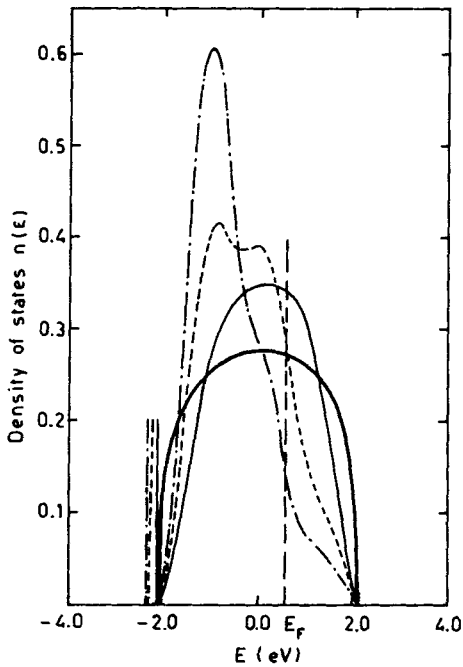
**Figure 2.** The modified surface-surface transfer functions near an atom chemisorbed on the 0th site of the cluster shown in figure 1.  $x$  indicates site of chemisorption.

### 3. Results and discussions

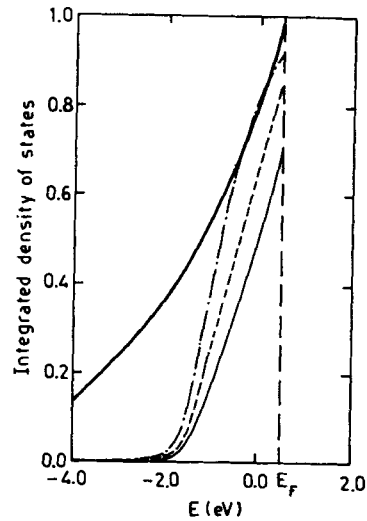
The important parameters characterising the present chemisorption system are  $V$ ,  $V_1$ ,  $\epsilon_m$  and  $\epsilon_a$ .  $V_1$  is kept as an adjustable parameter.  $V$  is calculated from the metal  $d$  bandwidth through the relation  $V = W/4(Z - 1)^{1/2}$ , where  $Z = Z_0 + 2Z_1$ , the bulk coordination number. Experimentally, the  $d$  bandwidth  $W$  cannot be uniquely known as the accurate experimental methods like ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) give the general band structure including the  $s$ - $p$  band; and it is difficult to separate out the contribution from the  $s$ - $p$  band. However with the help of theoretical model calculations it is possible to find out the contribution from the  $s$ - $p$  band and hence the  $d$  bandwidth. For Ni there are several band calculations (Stocks *et al* 1971; Hodges *et al* 1972; Watson and Bennett 1978; Moruzzi *et al* 1978; Wang and Callaway 1977) giving the  $d$  bandwidth a value between 4.2 and 4.8 eV. For the present work we consider the value 4.3 eV. For  $\epsilon_m$  and  $\epsilon_a$  we consider the value  $-10.6$  eV and  $-10.5$  eV respectively. It is to be noted that in the present chemisorption study using the scheme of Einstein and Schrieffer (1973) the results would not be very much sensitive to the values of  $\epsilon_m$  and  $\epsilon_a$ . Rather, it is the value of metal-adsorbate interaction,  $V_1$ , which plays a crucial role in determining the chemisorption properties. This is because, depending on the strength of this interaction split-off states may or may not appear below the band and corresponding change will take place in the shape of the band. In the present calculation the  $3d$  energy level is taken at the centre of the band. The Fermi energy is considered to be the energy at which the integrated bulk density of states is one. With respect to the centre of the band the Fermi surface appears at 0.55 eV. Some of the results of this calculation are presented in table 1. In figures 3–5 we plot different physical quantities for  $V_1 = 1.75$  eV. The density of states curves for a surface atom before and after chemisorption at different sites are shown in figure 3. In this figure the positions of the split-off states below the band are shown by straight lines (the split-off states which appear above the band are not shown in the figure). The integrated density of states is shown in figure 4. The chemisorption energy as a function of band filling is shown in figure 5. The centre hollow site is the most probable site of chemisorption in agreement with the experimental results (Andersson 1978). In figure 6 is shown the dependence of  $E_c$  on  $V_1$ . From this figure also we can find out the site of chemisorption if we know the experimental  $E_c$  value. We have to use the following argument: Our assumption of degenerate  $d$  band for the metal introduces some kind of spherical symmetry for the  $d$  orbitals. The interaction with H1s orbital may be thought to have the nature of a sigma bond so that in the present

**Table 1.** Chemisorption energy and other related quantities as a function of  $V_1$  (System: H/Ni).

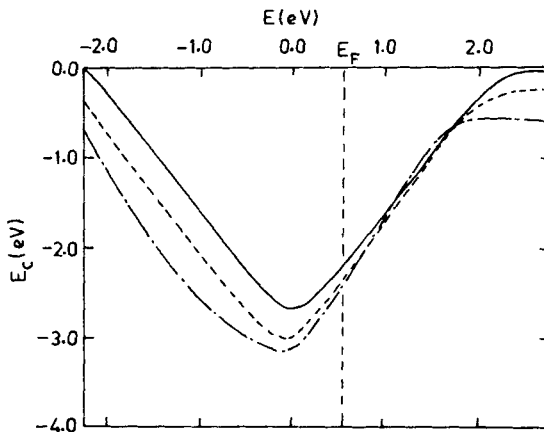
$V_1$ (eV)	Split-off states energies (eV)			Chemisorption energies (eV)		
	$E_s(A)$	$E_s(B)$	$E_s(C)$	$E_c(A)$	$E_c(B)$	$E_c(C)$
1.00	-0.10	-0.75	-0.70	-0.86	-0.75	-0.57
1.25	-1.35	-1.77	-1.98	-1.27	-1.16	-0.98
1.50	-1.88	-1.92	-2.18	-1.72	-1.62	-1.60
1.75	-2.12	-2.26	-2.35	-2.17	-2.34	-2.37
2.00	-2.30	-2.46	-2.57	-3.08	-3.20	-3.26



**Figure 3.** Density of states (DOS) of a surface atom after chemisorption at top position (—), at bridge position (---), and at the centre hollow position (-·-·-). (—) bulk DOS.

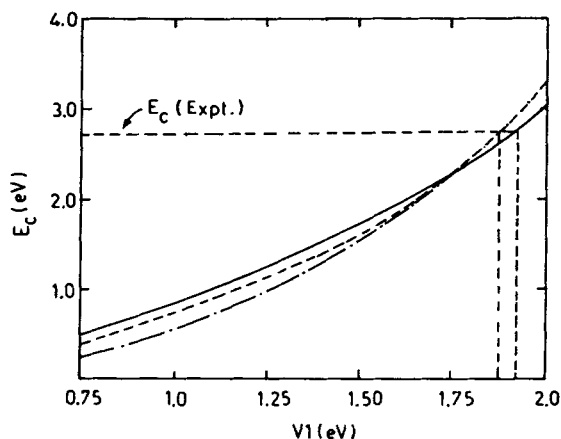


**Figure 4.** Integrated density of states for chemisorption. See figure 3 for description of curves.



**Figure 5.** Chemisorption energy as a function of band filling for chemisorption. See figure 3 for description of curves.

calculation the hopping interaction  $V_1$  is a function of the overlap of metallic  $d$  orbital and hydrogen  $1s$  orbital. As an adatom approaches the metal,  $V_1$  grows and if the site of adsorption is assumed to be the one for which  $V_1$  corresponding to the experimental value of  $E_c$  (Ertl 1979) is lowest, then we can conclude that the centre hollow position is the most probable site of the chemisorption. Unfortunately, in figure 6 this is not clearly



**Figure 6.** Chemisorption energy as a function of  $V_1$  for chemisorption. See figure 3 for description of curves.

resolved from the curve corresponding to bridge position near  $V_1 = 1.75$  eV; but the numerical values presented in table 1 clearly shows the difference:

#### 4. Conclusions

The simple TBCBLM has been used to study H chemisorption on Ni surface. The metal  $d$  band is represented by a five-fold degenerate band and the  $s$ - $p$  band is neglected altogether. Furthermore, we have not used the more accurate Hubbard-Anderson Hamiltonian to calculate self-consistently the chemisorption properties. However, the general effect of the correlations like raising the adatom ionisation level by an order of  $\approx 3$  eV has been considered in the calculation. We find that although some of these assumptions are very drastic, reasonably good agreement with experimental results has been achieved.

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