

Transfer Matrix Treatment of Atomic Chemisorption on Transition Metal Surface*†

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We study the atomic adsorption of hydrogen on paramagnetic nickel 100 surface, using the Green's function formalism and the transfer matrix technique, which allows the treatment of the geometry of the system in a simple manner. We incorporate electronic correlation at the adatom orbital in a self consistent Hartree-Fock approach. The adsorption energy, local density of states and charge transfer between the solid and the adatom are calculated for different crystal structures (sc and fcc) and adatom positions at the surface. The results are discussed in comparison with other theories and with available experimental data, with satisfactory agreement.

Estudamos a adsorção de hidrogênio atômico em níquel paramagnético, usando o formalismo de funções de Green e a técnica de matriz de transferência, que permite o tratamento da geometria do sistema de maneira simples. Através de uma aproximação auto-consistente de Hartree.

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-Fock, incorporamos a correlação eletrônica no orbital do átomo adsorvido (adatom). A energia de adsorção, a densidade local de estados e a transferência de carga entre o sólido e o adatom são calculadas para diferentes estruturas cristalinas (sc e fcc) e localizações diversas do adatom na superfície. Os resultados obtidos são discutidos em comparação com outras teorias e com dados experimentais, sendo o acordo satisfatório.

1. INTRODUCTION

A large theoretical effort is being directed in the last years towards a better understanding of the chemical and physical properties of chemisorbed systems. Not only is the problem challenging from the theoretical point of view, since it involves both surface and impurity techniques, but it is also of fundamental importance in material science and in processes such as catalysis, electron emission, vacuum techniques and preparation of "clean" surfaces.

Several models have been proposed for the chemisorption problem. News¹ uses a Green's function method with correlation effects at the adatom included via an Anderson term in the Hamiltonian and treated in the Hartree Fock approximation. Lyo and Gomer² use the same model, including the nonorthogonality between metallic and adsorbate wave functions and also screening effects in a phenomenological manner. Anda *et al*³ go beyond, considering correlation effects in the Hubbard⁴ instead of Hartree Fock scheme. Ying *et al*⁵ develop a density-functional theory in a self-consistent linear-response approach which allows full electrostatic self consistency. Einstein and Schrieffer⁶ suggest a molecular orbital treatment and Schrieffer and Gomer⁷ propose an induced covalent bond mechanism similar to the Heitler-London approach to describe adsorption.

A common aspect in the above mentioned treatments is the difficulty to incorporate in a simple manner the bulk structure and the adatom position relative to the surface. Most formalisms require explicit previous knowledge of the clean substrate Green's function or dispersion relation^{2,3,6}; the bulk is sometimes simulated by a linear

chain^{1,3}, by the "jellium" model⁵ or by an oversimplified surface density of states².

Fassaert and van der Avoird⁹ performed careful LCAO numerical studies for hydrogen layer adsorption on Nickel applied to finite crystals, and determine the stability of adsorption with respect to different substrate and adsorbate geometries. However correlation effects are not included in a self consistent manner, but are simulated by modifying the hydrogen ionization energy from 13.6 eV to 10 eV, which may be justified for chemisorbed layers, but not for a single ad-atom.

It is our aim in this work to present a simple model calculation for the chemisorption problem, in which both the crystal structure of the substrate and the adsorption site are taken into account. Our tight binding model Hamiltonian is similar to the one proposed for the treatment of hydrogen impurities in insulators⁹, with correlation effects at the impurity treated self consistently in the Hartree-Fock approximation, which is equivalent to Newns' treatment¹. We develop a Green's function theory based on the transfer matrix technique^{10,11}; (which is similar in some respect to the method of moments¹² and to the continued fraction method¹³), and we are able to incorporate the real structure of the semi-infinite crystal as well as the ad-atom position at the surface in a natural way.

In Sec.2 we introduce the model Hamiltonian and obtain the Green's function matrix elements by the transfer matrix technique. A simple expression for the adsorption energy is developed in Sec. 3. In Sec. 4 we estimate numerical values for the parameters appearing in the Hamiltonian to describe hydrogen chemisorption in nickel, and discuss the nature of the self consistent solutions for the problem. In Sec. 5 our main results are presented and compared with experiment and with other theories. The local density of states of the ad-atom basically agrees with previous treatments, but we get a charge transfer from the bulk to the ad-atom of about 0.1e, which is smaller than Newns's result¹ and in agreement with more elaborate treatments³ and with experimental evidence.

2. THE HAMILTONIAN AND THE GREEN'S FUNCTION

We restrict ourselves to the problem of one isolated atom (ad-atom) on a transition metal surface. In the tight binding one-electron approximation, we assume for simplicity one isotropic orbital per site to form a complete orthonormal basis set for the semi-infinite substrate plus ad-atom system. Of course the transition metal d electrons play a fundamental role in the chemisorption mechanism, therefore in the numerical application we take parameters that reproduce the characteristics of the $3d$ transition metal band.

In the localized basis set $\{|\alpha, \sigma\rangle, \{|i, \sigma\rangle\}\}$, where α represents the ad-atom, i represents a general substrate site, and σ is the spin index, our model Hamiltonian is written as:

$$H = \sum_{\alpha} \Lambda_{\sigma} c_{\alpha\sigma}^{\dagger} c_{\alpha\sigma} + \sum_{i, \sigma} \Lambda c_{i\sigma}^{\dagger} c_{i\sigma} + \sum_{i, j} \sum_{\sigma} V c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_{\Delta, \sigma} V_{\alpha} c_{\alpha\sigma}^{\dagger} c_{\Delta\sigma} \quad (1.a)$$

nearest
neighbors

with

$$\Lambda_{\sigma} = E_I + \frac{1}{2} U \langle c_{\alpha\bar{\sigma}}^{\dagger} c_{\alpha\bar{\sigma}} \rangle = E_I + \frac{1}{2} U n_{\bar{\sigma}} \quad (1.b)$$

where $c_{\ell\sigma}^{\dagger}$ creates an electron in the spin orbital $|\ell, \sigma\rangle$, ℓ being a substrate or ad-atom site.

The first term in the Hamiltonian describes the ad-atom orbital self energy and correlation effects in the Anderson scheme¹⁴. In Eq. (1.b), E_I is the ad-atom ionization level, U is the intra-atomic Coulomb repulsion and $n_{\bar{\sigma}}$ ($n_{\bar{\sigma}}$) is the occupation number associated to spin $\bar{\sigma}$ ($\bar{\sigma} = -\sigma$) of the ad-atom orbital. In our model, $n_{\bar{\sigma}}$ is determined self consistently (see Eq. (27) and (28) below) and correlation effects are considered only at the ad-atom. The second and third terms are associated to the substrate: the self energy Λ defines the energy origin, and the nearest neighbors hopping integral V is associated to the transition metal $3d$ bandwidth. Relaxation effects due to the

surface can be incorporated by taking different values of A for surface and bulk layers¹¹, but we neglect this effect here. The last term in (1) describes the ad-atom-substrate coupling; the sum in A runs over the ad-atom nearest neighbor sites only.

In order to incorporate the substrate translational symmetry parallel to the surface xy plane explicitly in the formalism, we define two dimensional Bloch functions:

$$|n, \vec{k}, \sigma\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{i}(n)} e^{i\vec{k} \cdot \vec{R}_{\mathbf{i}}} |i, \sigma\rangle \quad (2)$$

where the sum is performed over the N sites $\vec{R}_{\mathbf{i}}$ of the n -th layer, ($n=0,1,2,\dots$) and \vec{k} belongs to the corresponding two dimensional Brillouin zone (B.Z.). The layer index corresponds to the real space z direction, and runs from $n=0$ at the surface plane to $n=\infty$.

We perform a basis transformation, from the fully localized set into the hybrid set:

$$\{|b_i\rangle\} = \{|a, \sigma\rangle, \{|n, \vec{k}, \sigma\rangle\} \quad (3)$$

in which the matrix elements of H given by (1) are easily calculated:

$$\langle a, \sigma | H | a, \sigma' \rangle = \Lambda_{\alpha} \delta_{\sigma\sigma'} \quad (4)$$

$$\langle a, \sigma | H | n, \vec{k}, \sigma' \rangle = V_{\alpha} f(\vec{k}) \delta_{n,0} \delta_{\sigma\sigma'} \quad (5)$$

$$\begin{aligned} \langle n, \vec{k}, \sigma | H | n', \vec{k}', \sigma' \rangle = & \{ [\Lambda + S_n(\vec{k})V] \delta_{nn'} + V[L_n^+(\vec{k}) \delta_{n',n+1} + \\ & + L_n^-(\vec{k}) \delta_{n',n-1}] \} \delta(\vec{k}-\vec{k}') \delta_{\sigma\sigma'} \quad (6) \end{aligned}$$

The form factor:

$$f(\vec{k}) = \frac{1}{\sqrt{N}} \sum_{\Delta} e^{i\vec{k} \cdot \vec{R}_{\Delta}} \quad (7)$$

with \vec{R}_{Δ} running over the ad-atom nearest neighbors position vectors re-

lative to the ad-atom site, depends on the position of the ad-atom projected at the $n=0$ layer. The quantities $S(\vec{k})$ and $L(\vec{k})$ and characteristic of the substrate structure:

$$S_n(\vec{k}) = \sum_m e^{i\vec{k} \cdot \vec{R}_m} \quad (8)$$

$$L_n^\pm(k) = \sum_{p(\pm)} e^{i\vec{k} \cdot \vec{R}_p(\pm)} \quad (9)$$

where the summations are performed over the relative position vectors of a given crystalline site of the n -th layer and its first neighbors: the index m refers to neighbors on the same layer (n) while $p(+)$ and $p(-)$ refer to layers $(n+1)$ and $(n-1)$ respectively.

We consider below both sc and fcc structures, for which:

$$S(\vec{k}) = 2 \left[\cos(d k_x) + \cos(d k_y) \right] \quad (10.a)$$

and

$$L^+(\vec{k}) = L^-(\vec{k}) = L(\vec{k}) = \begin{cases} 1, & \text{s.c.} \\ 4 \left[\cos\left(\frac{ax}{2}\right) \cos\left(\frac{dk_y}{2}\right) \right], & \text{f.c.c.} \end{cases} \quad (10.b)$$

where d is the lattice parameter of the *two dimensional* square lattice. Notice that for these structures the factors have no explicit n -dependence, and therefore we drop this subscript.

We are interested in calculating the Green's function, whose matrix elements relative to basis set (3) satisfy Dyson's Equation:

$$E \langle b_i | G | b_j \rangle = \delta_{ij} + \sum_m \langle b_i | H | b_m \rangle \langle b_m | G | b_j \rangle \quad (11)$$

Using eq. (4)-(6), we obtain the equations corresponding to the diagonal element relative to the ad-atom orbital:

$$(E - \Lambda_\sigma) \langle a, \sigma | G | a, \sigma \rangle = 1 + V_\alpha \sum_{\vec{k}} f(\vec{k}) \langle 0, \vec{k}, \sigma | G | a, \sigma \rangle \quad (12.a)$$

$$A(\vec{k}, E) \langle 0, \vec{k}, \sigma | G | a, \sigma \rangle = V_a f^*(\vec{k}) \langle a, \sigma | G | a, \sigma \rangle + L(\vec{k}) V \langle 1, \vec{k}, \sigma | G | a, \sigma \rangle \quad (12.b)$$

$$A(\vec{k}, E) \langle n, \vec{k}, \sigma | G | a, \sigma \rangle = L(\vec{k}) V \langle n+1, \vec{k}, \sigma | G | a, \sigma \rangle + \langle n-1, \vec{k}, \sigma | G | a, \sigma \rangle \quad n \geq 1, \quad (12.c)$$

with

$$A(\vec{k}, E) \equiv E - \Lambda - S(\vec{k}) V \quad (12.d)$$

This infinite set of coupled equations may be solved by introducing the transfer function:

$$T(\vec{k}, E) = \frac{\langle n, \vec{k}, \sigma | G | b, \sigma \rangle}{\langle b-1, \vec{k}, \sigma | G | b, \sigma \rangle}, \quad n \geq 1 \quad (13)$$

where $|b, \sigma\rangle$ is any element in (3) with spin σ , since (12.c) is still valid if $|a, \sigma\rangle$ is substituted by $|b, \sigma\rangle$. From eq. (13) and (12.c) a second order equation for T is obtained, whose solutions are:

$$T(\vec{k}, E) = \frac{A(\vec{k}, E) \pm \sqrt{A(\vec{k}, E)^2 - 4V^2 L(\vec{k})^2}}{2L(\vec{k}) V} \quad (14)$$

where the choice of sign is discussed below eq. (20).

Using eq. (13) in (12.a,b), we get

$$\langle a, \sigma | G | a, \sigma \rangle = \left[E - \Lambda_\sigma - V_a^2 \sum_{\vec{k}} \frac{|f(\vec{k})|^2}{[E - \Lambda - S(\vec{k}) V - T(\vec{k}) L(\vec{k}) V]} \right]^{-1} \quad (15)$$

from which the local density of electronic states per spin at the ad-atom may be obtained:

$$D_a^\sigma(E) = -\frac{1}{\pi} \text{Im} \langle a, \sigma | G | a, \sigma \rangle + \sum_{\lambda} \left(\text{res}_{E=E_\lambda} \langle a, \sigma | G | a, \sigma \rangle \right) \delta(E - E_\lambda) \quad (16)$$

where the summation is performed over all poles of $\langle a, \sigma | G | a, \sigma \rangle$.

By a similar procedure, any matrix element of G may be obtained. In particular:

$$\langle \alpha, \sigma | G | 0, \vec{k}, \sigma \rangle = V_{\alpha} f(\vec{k}) B(\vec{k}) \langle \alpha, \sigma | G | \alpha, \sigma \rangle \quad (17. a)$$

with

$$B(\vec{k}) = [A(\vec{k}) - T(\vec{k}) L(\vec{k}) V]^{-1} \quad (17. b)$$

and

$$\langle 0, \vec{k}, \sigma | G | 0, \vec{k}, \sigma \rangle = B(\vec{k}) [1 + V_{\alpha} |f(\vec{k})|^2 B(\vec{k}) \langle \alpha, \sigma | G | \alpha, \sigma \rangle] \quad (18)$$

The spectral density of states per spin at layer \underline{n} is¹¹

$$D_{n\vec{k}}^{\sigma} = -\frac{1}{\pi} \text{Im} \langle n, \vec{k}, \sigma | G | n, \vec{k}, \sigma \rangle + \sum_{\lambda} (\text{res}_{E=E_{\lambda}} \langle n, \vec{k}, \sigma | G | n, \vec{k}, \sigma \rangle) \delta(E - E_{\lambda}) \quad (19)$$

and the total density of electronic states of the syste, is given by:

$$D(E) = \sum_{\alpha} \left[D_{\alpha}^{\sigma}(E) + \sum_{n\vec{k}} D_{n\vec{k}}^{\sigma}(E) \right] \quad (20)$$

The sign of the square root in eq. (14) is chosen so as to satisfy the proper boundary and asymptotic conditions, namely

$$\lim_{|E| \rightarrow \infty} |T(\vec{k}, E)| \leq 1 \text{ and } D_{nk}^{\sigma}(E) \geq 0, D_{\alpha}^{\sigma}(E) \geq 0$$

which yields a positive sign for $E < (A + \delta(\vec{k})V - 2L(\vec{k})V)$ and a negative sign otherwise.

Notice that $T(\vec{k}, E)$, and therefore G , is imaginary in the energy interval $|A^2 - 4V^2L^2| < 0$, where the argument of the square root is negative; since this is the interval corresponding to the continuum or band states, the band edges for a given spectral density of states are easily obtained:

$$E_{\text{b.e.}}(\vec{k}) = A + V [S(\vec{k}) \pm 2L(\vec{k})] \quad (21)$$

and from eq. (10.a,b) the complete continuum range for the considered structures is given by:

$$E_{b.e.} = \begin{cases} A \pm 6V & , \text{ sc} \\ A + 4V \pm 8V & , \text{ fcc} \end{cases} \quad (22)$$

3. ADSORPTION ENERGY

The energy change of the system due to the adsorption process, ie, due to the "activation" of the ad-atom-substrate coupling V_a is:

$$\Delta W = \sum_{\sigma} \int_{-\infty}^{E'_F} E D_f^{\sigma}(E) dE - \sum_{\sigma} \int_{-\infty}^{E_F} E D_i^{\sigma}(E) dE \quad (23)$$

where the first term describes the total energy of the system after chemisorption, and the second term is the energy of the unperturbed system described by Hamiltonian (11) with $V_a = 0$, which corresponds to an isolated atom in states $|\alpha, \sigma\rangle$ and the clean substrate. We call $D_f^{\sigma}(E)$ and $D_i^{\sigma}(E)$ the perturbed and unperturbed density of states, and E'_F and E_F the corresponding values of the Fermi level. The condition of conservation of total number of electrons together with the fact that $E'_F \approx E_F$ leads to²:

$$\begin{aligned} \Delta W &= \sum_{\sigma} \int_{-\infty}^{E_F} (E - E_F) [D_f^{\sigma} - D_i^{\sigma}] dE = \\ &= \sum_{\sigma} \int_{-\infty}^{E_F} (E - E_F) \left\{ D_{\alpha}^{\sigma}(E) + \sum_{\vec{n}\vec{k}} \left[D_{\vec{n}\vec{k}, f}^{\sigma} - D_{\vec{n}\vec{k}, i}^{\sigma} \right] \right\} dE - (E_I - E_F) \quad (24) \end{aligned}$$

We assume that the only relevant contribution to ΔW from the summation $\sum_{\vec{n}\vec{k}} [D_{\vec{n}\vec{k}, f}^{\sigma} - D_{\vec{n}\vec{k}, i}^{\sigma}]$ is due to the $n=0$ (surface) term, therefore we neglect the contributions due to the energy change of the inner layers, which is a reasonable approximation⁸, and we get:

$$\Delta W = \sum_{\sigma} \int_{-\infty}^{E_F} (E - E_F) \left\{ D_{\alpha}^{\sigma}(E) + \left[D_{0\vec{k},f}^{\sigma} - D_{0\vec{k},i}^{\sigma} \right] \right\} dE + E_F - E_I \quad (25)$$

4. HYDROGEN CHEMISORPTION IN NICKEL

The experimental parameters for Ni relevant to our model are listed in Table I. If we choose the center of the 3d band as the zero of energy, the appropriate values of A and V according to eq. (22) and to the experimental band width are given in Table II for the scandfcc structures. The ionization energy of hydrogen is $I = 13.6$ eV and the intra-atomic correlation is $U = 12.9$ eV; the ionization level properly referred to the energy origin at the center of the band is given by $E_I = -I + \phi + E_F = -7.34$ eV. The only free parameter in our calculation is V_a , the hopping integral between the ad-atom and one of its nearest neighbors.

B.W.	E_F	ϕ	ΔW
3.8	1.76	4.50	-2.89

Table I - Experimental values for the 3d band with (B.W.), Fermi level measured from band center (E_F), work function (ϕ) and adsorption energy (ΔW) of Nickel, as quoted in ref.1. All energies are given in eV.

	A	V
sc	0	0.32
fcc	-0.95	0.24

Table II - Values in eV of the tight binding parameters for the substrate.

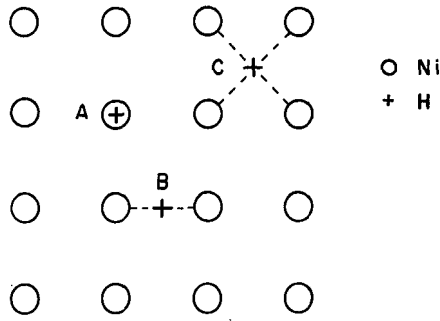


Fig.1 - Adsorption sites considered for H on Ni 100 surface.

We consider three different possibilities for the adsorption site, as shown in Fig.1: they are denoted as A (atop), B (bridge) and C (centered). For each of these geometries, the form factor given in eq.(7) satisfies:

$$|f_A(\vec{k})|^2 = 1/N \tag{26. a}$$

$$|f_B(\vec{k})|^2 = 2(1+\cos k_x d)/N \tag{26. b}$$

$$|f_C(k)|^2 = 4(1+\cos k_x d)(1+\cos k_y d)/N \tag{26. c}$$

For a fixed geometry and a given value of V_a , the average occupation per spin is easily obtained^{1,2}:

$$n_\sigma = \int_{-\infty}^{E_F} D_\alpha^\sigma(E) dE = F(n_\sigma) \tag{27}$$

therefore, the self consistency conditions which determine $(n_\sigma, n_{-\sigma})$ are:

$$\begin{aligned} n_\sigma &= F(n_{-\sigma}) \\ n_{-\sigma} &= F(n_\sigma) \end{aligned} \tag{28}$$

Two physically distinct situations may occur: magnetic ($n_\sigma \neq n_{-\sigma}$) and non magnetic ($n_\sigma = n_{-\sigma}$) solutions. Non magnetic solutions exist for all V_a , while magnetic solutions are found only up to a certain maximum value V_{max} of V_a , which depends on the particular geometry. The self-consistent solution of eq.(28) for sc structure, atop adsorption and three different values of V_a is presented in Fig.2. No-

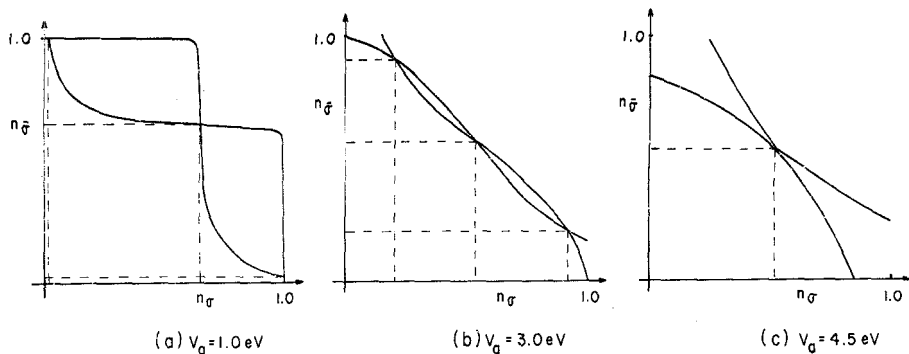


Fig.2 - Self consistent calculation for (n_α, n_β) , A-adsorption on sc substrate, for different values of V : a) $(n_\alpha, n_\beta) = (1.00, 0.03)$ or $(0.65, 0.65)$; b) $(n_\alpha, n_\beta) = (0.90, 0.21)$ or $(0.55, 0.55)$; c) $n_\alpha = n_\beta = 0.53$. In a) and b) $V_\alpha < V_{\max}$ and in c) $V_\alpha > V_{\max}$.

tice that while V increases, the two degenerate magnetic solutions merge continuously into the non magnetic one. Values of V_{\max} for four different geometries are given in Table III.

We perform the summations in the two dimensional B.Z. by the special points technique suggested by Cunningham¹⁵. We obtain 1% precision in the poles and residues of $D_\alpha(E)$ using 136 special points.

Substrate structure	sc			fcc
	A	B	C	A
V_{\max} (eV)	3.40	2.60	1.55	4.15
V_α^{fit} (eV)	3.70	2.85	1.90	4.30
$\Delta q/e$	0.08	0.10	0.12	0.07

Table III - V_{\max} (value of V_a above which only non magnetic solutions exist), V_α^{fit} (value of V_a which reproduces the experimental adsorption energy) and calculated excess ad-atom charge in electron ($\Delta q/e$) for different geometries.

5. RESULTS AND DISCUSSIONS

The adsorption energy for hydrogen chemisorption on Nickel 100 surfaces is easily calculated from expression (25). The results are presented in Fig.3 for four different geometries as a function of the parameter V_a . Notice that when a magnetic solution exists, it is associated to a bound state which is always lower in energy than the corresponding non magnetic solution. For a fixed value of V_a and for a given crystal structure, we obtain $\Delta W(C) < \Delta W(B) < \Delta W(A)$, indicating a stronger binding with increasing number of the ad-atom first neighbors, as expected. On the other hand, ΔW is a strongly decreasing function of V_a , and the $3d$ wavefunctions spatial characteristics suggest that $V_a(A) > V_a(B) > V_a(C)$, therefore the stability criterium above may be inverted, as is actually obtained in LCAO studies⁵ which indicate a greater stability for the A-position in H layers adsorption in Nickel.

In all cases, the experimental value of ΔW may be fitted by a value $V_a = V_a^{fit}$, (given in Table III), for which only the non magnetic solution exists, which is in agreement with previous models^{1,2,3}. Notice that V_a^{fit} is typically bigger than V by one order of magnitude, which implies that the H-Ni nearest neighbors equilibrium distance is smaller than the Nickel lattice parameter, in agreement with LCAO studies⁸.

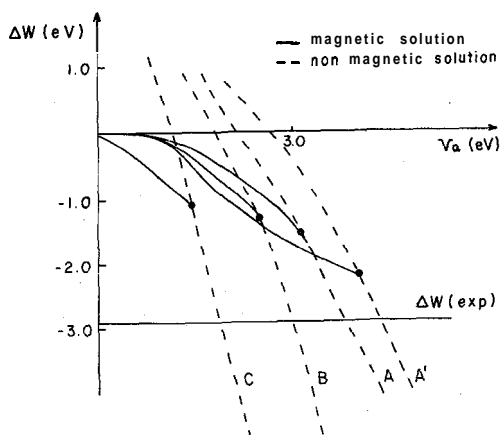


Fig.3 - Adsorption energy for sc substrate and Atop (A), Bridge (B), and Centered (C) adsorption sites and for fcc substrate, Atop adsorption (A').

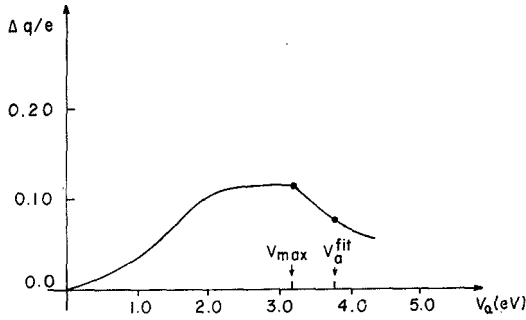


Fig.4- Excess adatom charge in electrons for A-adsorption in sc substrate

We have tested the stability of our results with respect to changes of ± 1 eV in A and ± 0.1 eV in V , which correspond to a maximum variation in the value of ΔV of 15%, and gives no qualitative change in the general behavior of ΔV as a function of V_a ,

The electronic charge transfer to the ad-atom, Aq , is simply related to the self consistent values of n :

$$\Delta q/e = n_{\sigma} + n_{\bar{\sigma}} - 1 \quad (29)$$

where e is the electron charge. The behavior of this quantity as a function of V_a is qualitatively the same for all geometries: it increases with V_a in the region where the magnetic solution exists, and in the non magnetic region it decreases with V_a . In Fig.4 we present the results for A-adsorption in sc substrate, which is in qualitative agreement with the results of News¹. The values of $\Delta q/e$ for $V_a = V_a^{fit}$ are presented in Table III, and indicate a charge transfer to the ad-atom of the order of $0.1 e$, which is considerably smaller than the results of News¹ $Aq = 0.16 e$, and Fassaert *et al*⁸ $\Delta q \sim 0.3 e$ and agrees with the results of Anda *et al*³. A large value for the charge transfer contradicts the experimental evidence given by the small change in the work function $\Delta\phi = 0.3$ eV¹⁶ due to H adsorption in Ni. We obtain smaller values for Aq in A-adsorption, which is an indication of the stability of that adsorption site with respect to the others, while the dependence is not very strong on the substrate structures examined, which is reasonable.

The local density of states at the ad-atom for fcc structu-

re, A-binding and $V_a = V_a^{\text{fit}} = 4.3$ eV is presented in Fig.5. Most of the density of states is concentrated in the localized states above and below the band. This is in qualitative agreement with Newns' result¹; quantitatively, the position of the pole below the band is in agreement with his result, while the pole above the band is about 1.5 eV higher in his calculation.

Finally we would like to mention that for all the physical quantities studied as a function of the ad-atom-substrate coupling V_a - namely the self consistent density of states, the adsorption energy and the charge transfer - the same general behavior is obtained for the crystal structures and adsorption sites considered, which allows us to consider V_a as a parameter which scales the physics of the system according to its geometry.

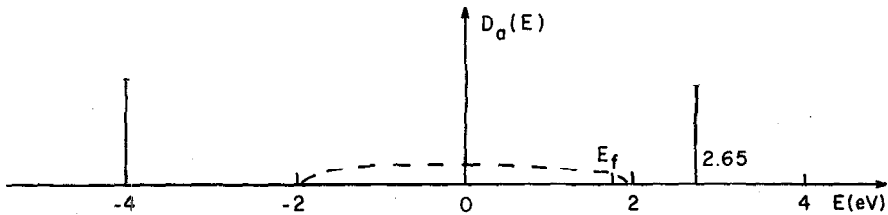


Fig.5 - Local density of states for H atop adsorption on Nickel, $V_a = V_a^{\text{fit}}$

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