LCAO STUDIES OF HYDROGEN CHEMISORPTION ON NICKEL
I. Tight-binding calculations for adsorption on periodic surfaces

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The model we have used to study hydrogen chemisorption on nickel surfaces is a tight-binding Extended Hückel method applied to finite (periodic) crystals up to about 250 atoms, the non-orthogonal basis set comprising five 3d orbitals, one 4s orbital and three 4p orbitals per atom. After calculating the band structure of fcc nickel, we have examined, by this model, the effect of the (100), (110) and (111) surfaces on the local density of states and the charge distribution. The results agree closely with moment calculations of the density of states in semi-infinite crystals and with experimental (XPS, UPS and INS) spectra. Extensive studies have been made of the influence of adsorption on the (partial) densities of states in order to illuminate the nature of the chemisorption bond. Particularly, we have concluded that both the 3d electrons and the conduction electrons take part in this bond. Equilibrium positions for adsorption on various sites have been determined and the adsorption energy has been computed and compared with experimental data. We find that the stability of adsorption decreases in the order (111) > (100) > (110) and Atop > Bridge > Centred.

1. Introduction

The last few years have shown a rapid increase in the number of quantum theoretical calculations on surfaces and adsorption stimulated mainly by the following two causes. From the experimental side an increasing amount of data become available from many different techniques, mostly spectroscopical, on single surfaces which are structurally well-defined, for instance, by simultaneous LEED studies. On the other hand, the computational methods for solids and molecules have advanced so far, that one is ready to attack the surface problem. Especially the surfaces of semiconductors and transition metals, in view of their practical interest, are studied quite intensively.

The quantum theoretical approaches to surfaces and adsorption can be divided into two categories. The first group of methods is based on a semi-infinite crystal model, the second group on model clusters of limited size.

The first model has been developed by Grimley [1], Koutecky [2] and others [3], and can now be applied to calculate adsorption energies, explicitly taking into account
the effect of electron repulsion on the adsorbed atom and some nearby surface
atoms [4–6]. This has been performed by Grimley and Pisani [4] in the Hartree–
Fock scheme and by Paulson and Schrieffer [6] in a Valence-Bond formalism. Al­
though one has found an elegant way to deal with the band structure of the under­
lying solid in the form of a Green function or resolvent, this treatment is still so
complicated that it has only been applied to hypothetical “cubium” crystals.
(Cubic crystals with one s-type orbital per atom, described by a tight-binding scheme
with only nearest neighbour interactions.) In applications to real d-electron systems
(transition metals) the form of the d-band was greatly oversimplified. For instance,
the density of d-states is replaced by a simple δ-function [7], a semi-elliptical dis­
tribution [8] or other approximations [9,10].

The only semi-infinite crystal studies which incorporate the real structure of the
d-band in fcc, bcc or hcp transition metals are those of Cyrot-Lackmann et al. [11–
15] and Heine [16], Haydock et al. [17–19]. They calculate the d-band density of
states by a moment expansion technique or by a continued-fraction expansion of the
(local) Green function. The d-band is described by a tight-binding scheme, and the
effect of the conduction electrons and d-band/conduction band hybridization are
neglected. When discussing our results, we refer in more detail to these calculations,
which also include some treatments of adsorption.

The second type of methods use a cluster model for the surface or adsorption site.
These methods which are now applied to clusters up to 30 light atoms such as carbon
or 15 transition-metal atoms, are the same as those used for large organic molecules
or transition-metal complexes: the Extended Hückel method [20], the CNDO method
[21] and the SCF Xα Scattered Wave method [22–24]. Although the semi-empirical
methods are always hampered by some arbitrariness in the choice of parameters, one
has collected so much material from molecular calculations by now, that a realistic
interpretation of the results is nevertheless possible. The main difficulty with these
limited-size clusters is that they should be embedded in a larger crystal with covalent
bonding occurring between the atoms. This embedding is usually omitted or simulated
by some artificial boundary conditions, the effects of which are not known.

The calculations presented in this paper provide a link between the two different
approaches of the surface problem. We have calculated finite crystals by the LCAO
or tight-binding method, approximating matrix elements over atomic orbitals by the
Extended Hückel scheme. This enables a direct comparison with cluster model re­
results. On the other hand, by imposing Born–Von Kármán periodic boundary condi­
tions on the crystal in directions parallel to the surface and transforming the secular
matrix to Bloch type “layer orbitals”, we have simplified the calculations to a large
extent. Thus, we have treated transition-metal crystals up to about 250 atoms, with
9 orbitals per atom. The periodicity imposed on the crystals prevents the occurrence
of undesired boundary effects and the crystal size permitted by this method is already
sufficient to calculate the band structure, the density of states, etc., which can be
compared with (semi-)infinite crystal results.

As a typical example of practical importance we have studied the adsorption of
hydrogen atoms on different low index surfaces of fcc nickel as a function of the adatom position. Besides the 3d orbitals, 4s and 4p orbitals have been included since we know that, via hybridization, they have an effect on the band structure [25] and, particularly, we have found also [26] that they can strongly take part in adsorption bonding. Therefore, it seems better to include these orbitals than to omit them completely [4-19], although we realize that a tight-binding description of the conduction bands does probably not optimally represent all physical properties of the metal. We have given particular attention to the adsorption energies on different sites and to the effect of surface formation and hydrogen adsorption on the (local) charge distribution and density of states. Besides the possibility of comparing our results with either of the two traditional approaches, we also gain some insight into the localized character of the adsorption bond.

2. Description of the method

2.1. The model

In order to test the tight-binding Extended Hückel method and its parametrization, we have first performed some calculations of the bulk band structure of fcc nickel. The non-orthogonal atomic orbital basis set \{i\chi_p(r - R_m); p = 1, ..., 9\}, five 3d, one 4s and three 4p orbitals localized on the centres \(R_m\), has been transformed into Bloch orbitals, after imposing Born–Von Kármán cyclic boundary conditions over \(N_1, N_2, N_3\) unit cells. In order to obtain the one-electron states of the crystal a 9-dimensional (complex arithmetic) secular problem can be solved for each wave vector \(k\) independently. Usually in solid state theory one takes \(N_i (i = 1, 2, 3)\) infinitely large and calculates, in principle, all \(k\) points in the first Brillouin zone [27]. In practice, the calculation of any physical quantity has to be performed by summation over a certain number of representative points. In our model, since we intend to calculate surface and adsorption effects on finite crystals, we have studied both infinite and finite \(N_i\). The latter choice corresponds to collecting a finite selection from the infinite crystal solutions, namely those Bloch waves of which the wave length is a divisor of the crystal dimensions. The effects of this selection are discussed.

For studying a specific surface plane, for instance (100), (110) or (111), we have chosen two of the lattice vectors, \(a_1\) and \(a_2\), parallel to this plane and simply omitted the cyclic boundary condition in the third, \(a_3\), direction. Thus we have produced a crystal with two parallel surfaces which consists of \(N\) layers. If \(N\) is sufficiently large, which has been verified in our calculations, it can be assumed that these surfaces do not influence each other. In our crystal the bulk structure is continued up to the surfaces, but it is very simple to include the effect of surface dilation as long as the two-dimensional unit cell \((a_1, a_2)\) is not perturbed. Also perturbations which double the unit cell dimensions, such as may occur by surface reconstruction or by half-monolayer adsorption, can be treated without too much difficulty.
We can benefit by the periodicity parallel to the surface if we introduce a basis of two-dimensional Bloch orbitals characterized by $k_\parallel = (k_1, k_2)$ and the layer number $m$ and solve the following $9N$-dimensional secular problems over these "layer orbitals":

$$\sum_{m=1}^{N} \sum_{q=1}^{9} \left[ H_{mp;mq}(k_\parallel) - e(k_\parallel) S_{mp;mq}(k_\parallel) \right] c_{mq}(k_\parallel) = 0 ,$$

(1a)

with

$$H_{mp;mq}(k_\parallel) = \sum_{m_1=1}^{N_1} \sum_{m_2=1}^{N_2} \exp[i(k_1 m_1 + k_2 m_2)]$$

$$\times \langle x_p(r - m_1 a_3)|H|x_q(r - m_1 a_1 - m_2 a_2 - m_3) \rangle,$$

(1b)

and a corresponding expression for the overlap matrix elements.

For studying hydrogen adsorption on the different nickel surfaces we have proceeded as follows. An adsorption site is characterized by an (arbitrary) position vector $a$ with respect to some surface atom. By means of the vectors $a_1$ and $a_2$ one generates a complete monolayer of hydrogen atoms on equivalent adsorption sites with the same periodicity as the surface. By adding one extra layer orbital characterized by the same $k_\parallel$, which is composed of hydrogen $1s$ orbitals, to the secular problem (1a), we describe the finite crystal with an adsorbed monolayer of hydrogen. This can easily be generalized to several monolayers and the resulting secular problems, with or without adsorption, can be solved by direct diagonalization or by invoking the resolvent methods of refs. [28, 29]. In practice, we have used the direct diagonalization method, except in some test cases, since these calculations involve a relatively small number of layers whereas the range of direct interactions between conduction band orbitals is rather large (see section 2.2). The resolvent method becomes advantageous when the number of layers is increased or nearest neighbour interactions are considered only.

2.2. Calculation of integrals

The overlap and $H$-matrix elements between atomic orbitals, which occur for instance in (1b), have been approximated by the Extended Hückel scheme, as we did in earlier cluster calculations [26]. The nickel nearest neighbour distance has been taken equal to 2.49 Å. The overlap elements $S_{pq}(R) = \langle x_p(r)|x_q(r - R) \rangle$ have been computed on the basis of Slater type orbitals, with double exponent for the 3d orbitals, single exponent for 4s and 4p, the exponents and contraction coefficients being given in table 1. We have assumed that the 4s and 4p orbitals in the nickel metal are somewhat less diffuse than in the free atom. For the hydrogen $1s$ orbital an exponent of 1.0 has been chosen, though we have performed some test calculations with a value of 1.2 which yielded quite similar results.
Table 1
Atomic orbitals and valence state ionization energies

<table>
<thead>
<tr>
<th></th>
<th>Exponents ($a_0^2$)</th>
<th>Contraction coefficients</th>
<th>VSIE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni 3d</td>
<td>5.75 2.00</td>
<td>0.5683 0.6292</td>
<td>-8.38</td>
</tr>
<tr>
<td>4s</td>
<td>2.1</td>
<td>1.0</td>
<td>-6.97</td>
</tr>
<tr>
<td>4p</td>
<td>2.0</td>
<td>1.0</td>
<td>-3.34</td>
</tr>
<tr>
<td>H 1s</td>
<td>1.0</td>
<td>1.0</td>
<td>-10.0</td>
</tr>
</tbody>
</table>

The diagonal $H$-matrix elements $H_{pp}(R = 0) = \langle x_p(r)|H|x_p(r) \rangle$ have been approximated for the nickel orbitals by Valence State Ionization Energies [30], assuming a valence state configuration in the metal of $3d^{9.4} 4s^{0.6}$ (see table 1). For hydrogen the neutral atom value is $-13.6$ eV, but this value would result in a considerable, non-physical electron transfer from nickel to hydrogen. This effect can be avoided by adjusting the orbital energies to the atomic charges in an iterative Extended Hückel calculation. This iterative method is more time consuming, however, and yields unsatisfactory results for the adsorption energy [26]. Therefore, we have chosen the simpler solution to use a modified VSIE of $-10.0$ eV for hydrogen only, since we expect that the single hydrogen orbital is more affected by charge transfer than the large bulk of nickel orbitals. In an iterative method this would correspond to a hydrogen charge of about $-0.3$ units, which is also the charge that we have actually found in our calculations. The experience of Anders et al. [31], who have also used this value and compared their results with iterative Extended Hückel calculations justifies our assumption. The non-diagonal elements

$$H_{pq}(R) = \langle x_p(r)|H|x_q(r-R) \rangle,$$

have been approximated by the Wolfsberg–Helmholz formula:

$$H_{pq}(R) = KS_{pq}(R)[H_{pp}(R = 0) + H_{qq}(R = 0)]/2,$$

with the usual value of $K = 1.75$.

Since the magnitude of these matrix elements $S_{pq}(R)$ and $H_{pq}^*(R)$ decreases with increasing interatomic distance $R$ it is not necessary to consider all atom pairs in the entire crystal. On the other hand, the inclusion of only nearest neighbour interactions appeared definitely insufficient for those elements involving $4s$ and $4p$ orbitals. We have found that a range of $2$ nickel nearest neighbour distances ($5.0$ Å) which allows every nickel atom in the bulk to interact directly with $4$ shells of neighbours ($54$ atoms), is satisfactory. The same range has been used for the nickel–nickel, the nickel–hydrogen and the hydrogen–hydrogen interactions. Increase of this range to $3$ nickel nearest neighbour distances ($176$ bulk atoms) yielded no visible improvement of the results. Once the matrix elements over atomic orbitals have been calculated, they are easily transformed into integrals over Bloch or layer orbitals [formula (1b)].
2.3. Adsorption energy

One of the quantities we have calculated is the adsorption energy per hydrogen atom. According to the usual Extended Hückel scheme this energy can be defined as:

$$\Delta E_{\text{ads}} = \left( \sum_i N_i^A \varepsilon_i^A - \sum_i N_i^C \varepsilon_i^C \right) / N^H - e^H,$$

where $\varepsilon_i^A$, $N_i^A$ and $\varepsilon_i^C$, $N_i^C$ are the orbital energies and occupation numbers for the finite crystal, with and without hydrogen adsorption, respectively, $N^H$ is the total number of hydrogen atoms and $e^H$ the energy of an isolated hydrogen atom. If the adsorption energy were thus calculated we would obtain a reasonable estimate in the neighbourhood of the chemisorption equilibrium positions. These positions are not known, however, particularly for adsorption over surface holes where the equilibrium heights cannot even be guessed reliably. Neither can they be calculated, because the Extended Hückel method often fails to predict an energy minimum as a function of the bond length. Therefore, the results would strongly depend upon rather arbitrary assumptions about the equilibrium positions unless we can improve our method to predict these positions correctly.

![Fig. 1. Effect of nickel core repulsion on the Extended Hückel binding energy of NiH.](image-url)
One reason for this defect of the Extended Hückel method is that it only accounts for the valence electrons. As we can observe from fig. 1 an Extended Hückel calculation of NiH including 3d, 4s, 4p on Ni and 1s on H predicts an ever increasing attraction in the range where the energy minimum should be. Including the fully occupied core orbitals 3s and 3p on Ni such a minimum is obtained. According to Anders et al. [31] we have fitted the (short range) core repulsion thus calculated by an exponential function, \( a \exp(-bR) \) with \( R \) being the Ni–H distance, and added this pairwise potential between the nickel and the hydrogen atoms to the adsorption energy calculated by (3).

2.4. Density of states, population analysis

In solid state physics the total density of states is usually calculated by summation over a large number of specific [32] or random [33] points in the Brillouin zone. For finite crystals we can also calculate this quantity directly from its definition by simply counting the number of levels per energy interval.

The local density of states is commonly defined by:

\[
\rho_p(\varepsilon) = \sum_i |c_{pi}|^2 \delta(\varepsilon - \varepsilon_i),
\]

where \( c_{pi} \) is the coefficient of a given localized basis orbital (an atomic or layer orbital) \( |\psi_p\rangle \) in the crystal orbital \( |\psi_i\rangle \). In case we have more than one orbital \( |\psi_p\rangle \) per atom, (4) defines the partial (local) density of states of type \( |\psi_p\rangle \); the total density of states is obtained by summation over \( p \). Although these definitions apply for an orthogonal basis set \( |\psi_p\rangle \) they can be transferred to a non-orthogonal basis as well [34]. Because of overlap contributions, we obtain then a quantity which does not add up to the total density of states when summed over the complete basis \( |\psi_p\rangle \). For this reason, we define instead for a non-orthogonal basis:

\[
\rho_p(\varepsilon) = \sum_i \left[ |c_{pi}|^2 + \sum_{q\neq p} \text{Re}(c_{pi}^*c_{qj}S_{pq}) \right] \delta(\varepsilon - \varepsilon_i),
\]

where \( S_{pq} \) is the overlap integral between the basis orbitals \( |\psi_p\rangle \) and \( |\psi_q\rangle \). When integrated up to the Fermi level this definition of \( \rho_p(\varepsilon) \) yields the Mulliken “gross orbital population”, whereas definition (4) would yield the “net orbital population” [35].

3. Results and discussion

3.1. The periodic nickel crystal

The results of our band structure calculations with interactions included up to fourth order neighbours (54 atoms) in the fcc lattice are plotted in figs. 2, 3 and 4. We have also allowed for interactions up to ninth order neighbours (176 atoms) but
this did not change the figures visibly. We have made the density of states curves somewhat less dependent on the finite number of levels, the specific choice of $N_1$, $N_2$, $N_3$ and the positions of the energy intervals in the histogram by applying the following smoothing procedure: for any interval of 0.1 eV we count the number of levels in the interval plus the number of levels in some neighbouring intervals multiplied by decreasing weight factors (0.09 : 0.24 : 0.34 : 0.24 : 0.09 according to a gaussian distribution).

We have found that the band structure is in fair agreement with the results of more elaborate band calculations on nickel, applying the tight-binding d-band plus nearly free electron conduction band model [25], the APW scheme [37] or the ab initio LCAO—SCF method [38,39]. The d-band is somewhat too narrow, although we have included 3d—4s—4p hybridization, and its position is somewhat too low relative to the conduction band. Also the Fermi level is found too low (—7.13 eV) in comparison with experimental values [40,41]. At first, we have tried to correct for these differences by adjusting the nickel VSIE’s in the Extended Hückel method, but it appeared that the relative populations of the 3d and conduction band became somewhat less realistic, $3d^{8.6}$ (4s 4p)$^{1.4}$, than the original populations, $3d^{9.2}$ (4s 4p)$^{0.8}$, and that the charge transfer effects when forming a surface became improbably large. Therefore, we have maintained the usual Extended Hückel parametrization. Anyway, we may notice that in the other band structure calculations of nickel the absolute position of the bands is not computed at all [25,37,39] or is too low as well [38], the Fermi level being at —6.69 eV in the latter case.

The partial density of states distributions in fig. 4 demonstrate that all d-orbitals
yield important contributions to the entire d-band, but that specifically the \( t_{2g} \) type d-orbitals show extra peaks at the bottom and the top of the band, the top peak being more pronounced. This is in accordance with the conclusion from other band calculations \([25,42]\) about a prominent peak of \( t_{2g} \) character at the top of the band, which causes the \( t_{2g} \) preference of the magnetic form factor in nickel \([43]\). There is also very close agreement between our results and the moment expansion calculations of Ducastelle and Cyrot-Lackmann \([12]\), which lead, for instance, to the conclusion that the "\( t_{2g} \) band" has a larger second moment than the "\( e_g \) band" in fcc crystals. These conclusions support the general notions about the non-bonding nature of the \( e_g \) orbitals and the bonding/anti-bonding character of the \( t_{2g} \) orbitals (although this difference should not be understood too strictly), but they do not justify the simplified band picture by Goodenough \([44]\).
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Fig. 4. Partial density of states for the $e_g$ and $t_{2g}$ orbitals in the d-band of fcc nickel (point group $O_h$).

Table 2
Gross orbital populations for the bulk crystal ($N_1 = N_2 = N_3 = 5$) and for the surface layer of different 5-layer crystals ($N_1 = N_2 = 5$); local coordinate systems have been used at the different surfaces, the $z$-axes perpendicular to the surface, the $x$- and $y$-axes as in fig. 8

<table>
<thead>
<tr>
<th></th>
<th>bulk</th>
<th>(100)</th>
<th>(110)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{z^2}$</td>
<td>1.913</td>
<td>1.928</td>
<td>1.925</td>
<td>1.907</td>
</tr>
<tr>
<td>$d_{x^2-y^2}$</td>
<td>1.913</td>
<td>1.946</td>
<td>1.884</td>
<td>1.827</td>
</tr>
<tr>
<td>$d_{xy}$</td>
<td>1.794</td>
<td>1.693</td>
<td>1.841</td>
<td>1.827</td>
</tr>
<tr>
<td>$d_{yz}$</td>
<td>1.794</td>
<td>1.914</td>
<td>1.912</td>
<td>1.935</td>
</tr>
<tr>
<td>$s$</td>
<td>0.668</td>
<td>0.694</td>
<td>0.680</td>
<td>0.733</td>
</tr>
<tr>
<td>$p_x$</td>
<td>0.042</td>
<td>0.048</td>
<td>0.040</td>
<td>0.048</td>
</tr>
<tr>
<td>$p_y$</td>
<td>0.042</td>
<td>0.048</td>
<td>0.048</td>
<td>0.048</td>
</tr>
<tr>
<td>$p_z$</td>
<td>0.042</td>
<td>0.026</td>
<td>0.020</td>
<td>0.038</td>
</tr>
</tbody>
</table>

From the orbital populations in table 2 it is easily calculated that the d-electrons in the metal have a slightly preferential $e_g$ character (41.6% compared with 40% in the free atom). Also this value agrees very well with the 42% calculated by Desjonquères and Cyrot-Lackmann [15]. The absolute orbital populations cannot be compared because these authors assume a total d-electron number of 9.

The density of states distributions which have been produced for finite, rather small numbers of unit cells, $N_1, N_2, N_3 = 5$ or 6, are not very different from the results obtained with the usual solid state techniques, where these numbers are infinitely large, in principle. It is interesting to note that the curves are relatively better when the $N_i$-values are different, because this leads to a larger number of indepen-
dent \( \mathbf{k} \)-points in the Brillouin zone, independent in the sense that they are not connected by point group symmetry operations. Since the results even for values as small as \( N_f = 5 \) give a good impression of the band structure (if one does not wish to interpret every individual small peak), we can confidently use these finite values for studying surface and adsorption effects. All further conclusions have been tested with respect to their \( N_f \)-dependence, moreover. The same smoothing procedure for the density of states curves has been used throughout this paper.

### 3.2. The surfaces (100), (110) and (111)

The nickel lattices we have calculated to study these surfaces are periodic in the directions parallel to the surface over \( 5 \times 5, 6 \times 6 \) or \( 7 \times 7 \) unit cells and consist of 5 or 6 layers. In fig. 5 the local densities of states in the surface layers are compared to the bulk densities from the periodic crystal and in figs. 6 and 7 the specific partial contributions to the d-band are analyzed. Table 2 shows the orbital populations at the surface and in the bulk.

![Fig. 5. Local densities of states in the (100) and (111) surface layers, compared with the bulk density of states in fcc nickel.](image-url)
The results from fig. 5 are in excellent agreement with the conclusions from moment calculations [11–19] and from experimental UPS [45], XPS [46] and INS [47,48] data: the total d-band width is unaltered by the presence of the surface, but the second moment of the density of states distribution is reduced by a smaller slope at the edges. The d-band adopts more the shape of one central peak. The moment calculations, which include only d-orbitals with nearest neighbour interactions, predict that the second moment of the surface density of states is proportional to $Z$, the number of nearest neighbours of a surface atom. Indeed, we have found a larger band width reduction for the (100) surface ($Z = 8$) that for the (111) surface ($Z = 9$).

The effects of the surface on specific d-orbital densities, which can be observed

![Diagram](image)

**Fig. 6.** Surface and adsorption effects on the partial local densities of states at the (100) surface. (a) Surface layer density of states of different 3d orbitals, denoted by the representation symbols of the point group $C_{4v}$; for comparison the bulk density of states is given. (b) Surface layer density of states of the 4s and 4p orbitals. (c) Local density of states in the adsorbed hydrogen layer, as compared to the density of states of an isolated H layer with the same periodicity.
(b) Energy distribution for hydrogen 1s in bulk and different surface adsorption configurations. Energy is given in eV.

(c) Energy distribution for hydrogen 1s in an isolated H-layer and different surface adsorption configurations. Energy is given in eV.
Fig. 7. Surface and adsorption effects on the partial local densities of states at the (111) surface. (a) Surface layer density of states of different 3d orbitals denoted by the representation symbols of the point group C\textsubscript{3v}. For comparison the bulk density of states is given. (b) Surface layer density of states of the 4s and 4p orbitals. (c) Local density of states in the adsorbed hydrogen layer, as compared to the density of states of an isolated H layer with the same periodicity.
in figs. 6 and 7, are quite well understandable if one remembers the former bonding character of these d-orbitals in the bulk (e_g or t_2g) and visualizes their orientation with respect to the surface. So, the orbitals protruding from the (100) surface, d_{x^2}, d_{y^2}, d_{xy}, are more strongly influenced than the orbitals lying in the surface plane, d_{x^2-y^2}, d_{xy}; the t_2g orbitals d_{xz}, d_{yz} and d_{xy} are more affected than the e_g orbitals, d_{x^2} and d_{y^2}. In case of the (111) surface, the local d_{z^2} orbital pointing perpendicularly out of the surface, which is written as (d_{xy} + d_{xz} + d_{yz})/\sqrt{3} in the bulk coordinate system (and thus belongs to the t_2g representation), is more influenced than the rest of the d-orbitals.

By integrating the partial density of states up to the Fermi level we have calculated the orbital occupation numbers in table 2. The latter give a direct measure of the asphericity of the d-electron charge distribution at the surface, which was recently calculated also by Desjonquères and Cyrot-Lackmann [15] using their moment expansion method. For the (100) surface where the results can be directly compared, they are in good agreement: the order of the occupation numbers is the same except for the very small difference between d_{x^2} and d_{xz}, d_{yz}; the significantly lower occupation of d_{xy} is obtained from both calculations. Note again that the absolute values differ because of Desjonquères and Cyrot-Lackmann’s assumption of 9 d-electrons. For the (110) and (111) surfaces the relative occupation numbers cannot be compared directly, since Desjonquères et al. have expressed the d-orbitals always in the bulk coordinate system, whereas we have used d-orbitals adapted to the local symmetry at the surface.

3.3. Adsorption

The different sites on which hydrogen atoms have been adsorbed at the (100), (110) and (111) surfaces are shown in fig. 8. They can be denoted as A (atop), B (bridge) and C (centred). At the (110) surface two bridge positions are possible, B-long and B-short; at the (111) surface we have adsorption over an octahedral hole, C-oct., or over a tetrahedral hole, C-tet., with a nickel atom lying directly below the surface. The two-dimensional periodicity involved 5 X 5, 6 X 6 or 7 X 7 unit cells, the number of nickel layers has been taken as 5 or 6. At each site the adsorption energy per hydrogen atom has been calculated according to the method of section 2.3 as a function of the height over the surface and plotted in figs. 9a, b, c. The binding energies, hydrogen atomic charges and overlap populations at the equilibrium positions are collected in tables 3, 4 and 5. In order to get a more detailed insight into the nature of the chemisorption bond, the effect of adsorption on the local densities of states at the surface and in the hydrogen layer have been included in figs. 6 and 7.

The adsorption energy for various sites agrees fairly well with experimental values: an adsorption energy of 23 kcal/mole for molecular hydrogen [49-52] corresponds to a binding energy of 2.75 eV for hydrogen atoms. This value changes little over a rather large range of surface coverages; for a discussion of the heat of adsorption at monolayer coverage as compared with the initial heat of adsorption we refer to
paper II. For comparable sites A, B or C, those surfaces are most favourable, (110) > (100) > (111), where the surface atoms have the smallest number of nearest neighbours. This seems to be at variance with the experimental results [49–52], which are nearly equal for the three low index faces. However, the differences in our calculated values are not very pronounced. Moreover, we find an opposite effect from the 3d and the conduction electrons, as can be observed from the overlap populations in table 5, so that, for instance, a slight overestimate of the conduction band contribution could explain this difference. For adsorption on different sites, we find that the stability decreases in the order A > B > C. The maximum stability of the A-position is confirmed by some experimental data for hydrogen on Raney nickel [53].

The same qualitative conclusions have already been drawn from our earlier cluster calculations [26], but the differences between A, B and C sites are less pronounced now we have calculated equilibrium positions (which are quite different from the ones we had assumed for C-sites). The comparison with more recent cluster calculations is given in paper II. Comparison with semi-infinite crystal calculations is difficult since those treatments which include real d-band systems [11–19] do not compute the adsorption energy, whereas other calculations are concerned with the hypothetical solid “cubium” [4,6,54,55] or other approximate models [7–10, 56]. The results of the latter calculations depend strongly on the parametrization and it is hard to say which parametrization corresponds with the actual system of hydrogen adsorbed on nickel.

The atomic charge on the hydrogen atoms according to Mulliken’s definition is
Fig. 9. Adsorption energy at different surfaces as a function of the height of the hydrogen atoms over the surface (including the repulsion with the nickel cores): (a) atop adsorption; (b) bridge adsorption; (c) centred adsorption.

found to have a maximum value for A-sites (about $-0.35$ unit charges) and to be somewhat smaller for B- and C-sites ($-0.30$ to $-0.25$ unit charges). The same effect
Table 3
Adsorption energies at equilibrium positions of the hydrogen atoms; distances are given with respect to the nearest surface Ni atom; periodicity \( N_1 = N_2 = 5 \)

<table>
<thead>
<tr>
<th></th>
<th>Ni–H distance (Å)</th>
<th>( \Delta E_{\text{ads}} ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 layers</td>
</tr>
<tr>
<td>(100)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1.50</td>
<td>-2.60</td>
</tr>
<tr>
<td>B</td>
<td>1.70</td>
<td>-2.50</td>
</tr>
<tr>
<td>C</td>
<td>1.91</td>
<td>-2.32</td>
</tr>
<tr>
<td>(110)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1.50</td>
<td>-2.80</td>
</tr>
<tr>
<td>B-short</td>
<td>1.70</td>
<td>-2.60</td>
</tr>
<tr>
<td>B-long</td>
<td>1.86</td>
<td>-2.48</td>
</tr>
<tr>
<td>C</td>
<td>2.19 ( ^a )</td>
<td>-2.38</td>
</tr>
<tr>
<td>(111)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>1.50</td>
<td>-2.46</td>
</tr>
<tr>
<td>B</td>
<td>1.70</td>
<td>-2.23</td>
</tr>
<tr>
<td>C-tet.</td>
<td>1.81</td>
<td>-2.18</td>
</tr>
<tr>
<td>C-oct.</td>
<td>1.81</td>
<td>-2.24</td>
</tr>
</tbody>
</table>

\( ^a \) The Ni–H distance for the Ni atom directly below the hole is 1.60 Å.

Table 4
H-atom charges at equilibrium positions; 5-layer crystals, \( N_1 = N_2 = 5 \)

<table>
<thead>
<tr>
<th></th>
<th>(100)</th>
<th>(110)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-ads.</td>
<td>-0.36</td>
<td>-0.41</td>
<td>-0.33</td>
</tr>
<tr>
<td>B-ads.</td>
<td>-0.30</td>
<td>{ -0.33 ( ^a )</td>
<td>-0.25</td>
</tr>
<tr>
<td>C-ads.</td>
<td>-0.25</td>
<td>-0.27</td>
<td>{ -0.23 ( ^b )</td>
</tr>
</tbody>
</table>

\( ^a \) B-short and B-long, respectively.
\( ^b \) C-tet. and C-oct., respectively.

was qualitatively found from cluster calculations [26]. The average magnitude of this hydrogen charge justifies the assumption of a hydrogen VSIE of \(-10.0\) eV (section 2.2) which corresponds rather well with a self-consistent result, although self-consistency has not been imposed.

From the partial density of states curves in figs. 6 and 7 we can clearly observe the interactions between the hydrogen orbitals and the nickel 3d, 4s and 4p orbitals. Some shifting and broadening of the hydrogen layer levels occurs and the positions of these peaks in the hydrogen density of states correspond with new peaks in the 3d, 4s and 4p densities of the metal caused by adsorption. Since the shifts of these peaks are relatively large compared with their broadening, one can hardly speak about "virtual" hydrogen levels [9]. This phenomenon points to a strong covalent bonding [57] of the hydrogen orbitals both to the conduction band orbitals 4s and 4p and to some of the 3d orbitals. Which specific d-orbitals take part in adsorption
Table 5
Overlap populations between an H atom (at equilibrium position) and the nearest surface Ni atom; 5-layer crystals, $N_1 = N_2 = 5$

<table>
<thead>
<tr>
<th></th>
<th>(100)</th>
<th>(110)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3d</td>
<td>0.066</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>4s + 4p</td>
<td>0.214</td>
<td>0.236</td>
</tr>
<tr>
<td>B</td>
<td>3d</td>
<td>0.039</td>
<td>0.035</td>
</tr>
<tr>
<td></td>
<td>4s + 4p</td>
<td>0.108</td>
<td>0.113</td>
</tr>
<tr>
<td>C</td>
<td>3d</td>
<td>0.023</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>4s + 4p</td>
<td>0.049</td>
<td>0.025</td>
</tr>
</tbody>
</table>

a B-short and B-long, respectively.
b Overlap population with the nearest surface atom and the atom directly below the hole, respectively.
c C-tet. and C-oct., respectively.

bonding is determined by the environment of the adsorption site, rather than by the properties of the isolated surface. For instance, one observes very clearly from fig. 6 that on the (100) surface the $d_{z^2}$ orbital mainly contributes to A-type adsorption, the $d_{xz}$, $d_{yz}$ combination to B-type and $d_{x^2-y^2}$ to C-type. (Note again that these d-orbitals are expressed in a local coordinate system with the z-axis perpendicular to the surface plane, as shown in fig. 8.) From fig. 7 it follows that for the A-site at the (111) surface it is also the local $d_{z^2}$, which is written in bulk coordinates as $(d_{xy} + d_{xz} + d_{yz})\sqrt{3}$, that yields the main contribution.

In relation to those models [58—60,15] which predict specific adsorption sites by considering the properties of the bulk metal or the isolated surface, we can make the following remarks. No specifically stable adsorption shows up on those sites, A and C at (100), where the interaction occurs with the former non-bonding ($e_g$) orbitals from the bulk. Neither those $t_{2g}$ orbitals which are protruding from the surface (“dangling bonds”), at the B-site on (100) or the A-site on (111), show any particular activity. Also the occupation numbers of specific d-orbitals at the free surface [15] do not represent a good measure for the adsorption stability (which is not surprising since hydrogen chemisorption is primarily covalent, even though some charge transfer takes place). On the contrary, it is the structure (symmetry) of the “surface molecule” $\text{Ni}_n\text{H}$ with $n = 1, 2, 3$ or 4 and its (direct) environment which determines the nature and relative stability of the chemisorption bond. More concrete information on the localized character of this bond is discussed in paper II.

Most calculations have been performed for a 5-layer nickel lattice with a $5 \times 5$ unit cell periodicity parallel to the surface. We have checked the conclusions from this model by repeating some of the calculations with 6 layers and $6 \times 6$ or $7 \times 7$
periodicity. The results of these tests demonstrate that the absolute adsorption ener­
gies vary a little, with the largest differences being found between odd and even
numbers of layers. For A-site adsorption on the (100) surface we find, for instance,
−2.56 eV for a 6 X 6 crystal, −2.64 eV for a 7 X 7 crystal as compared to −2.60 eV
for a 5 X 5 crystal with 5 layers; a 5 X 5 crystal with 6 layers yields the value of
−2.49 eV. The results of table 3 indicate, though, that all relative effects discussed
in this section are invariant to the size of the crystal. Also the adsorption of two
hydrogen layers on the opposite surfaces of a 5-layer crystal has not shown any
mutual effects, so that we may safely assume that the finite, rather small, dimensions
of our model systems do not significantly influence our conclusions for surface and
adsorption effects.

4. Conclusions

Summarizing the main conclusions from the preceding sections we can make the
following observations. Both the 3d electrons and the conduction electrons in the
4s—4p band of nickel take part in the chemisorption bond with hydrogen. Although
the effect of the 4s and 4p orbitals may be somewhat overemphasized by the Ex­
tended Hückel method, since this method is strongly based on overlap criteria, our
calculations do not justify the complete omission of the conduction electrons which
is a starting point in many calculations for adsorption on transition metals [4—19].
Still, in those calculations which include all five 3d orbitals on the nickel atoms
[11—19] the conclusions about surface effects on the d-band structure and on the
asphericity of the d-electron charge distribution agree very closely with our results.
Apparently, the neglect of d-band/conduction band hybridization does not affect
these (relative) conclusions. The agreement between these results is the more interest­
ing since our method (working in finite k-space with finite crystals) is quite different
from the approach of Cyrot-Lackmann et al. [11—15] and Haydock et al. [17—19]
(who use a semi-infinite crystal model and calculate the density of states by a con­
tinued-fraction expansion of the Green function). Unfortunately, not many results
for adsorption on transition metals are available yet from these authors.
The stability of adsorption on different low index planes, (100), (110) and (111),
increases with a decreasing number of nearest neighbours to the surface atoms. These
differences are not very pronounced, however. Different sites on the same surface,
show the following decrease in adsorption stability: A (atop) > B (bridge) > C (centred).
Finally it can be concluded that the stability and the nature of the chemisorption
bond on nickel is not so much determined by the properties of the bulk metal or by
the characteristics of the clean surface, but rather by the structure of the “surface
molecule”. This conclusion has been further elaborated by a comparison with cluster
calculations in paper II, where also the localization of the chemisorption bond and
the effect of the boundary conditions on the “surface molecule” are discussed.
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