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Total-energy calculations for surface reconstructions in adsorbate systems

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Abstract. The reconstructive effect of adsorbed atomic monolayers of carbon and nitrogen on a nickel {001} surface is well known. The work presented here calculates the covalent part of the total energy of such a system, with a 0.5 monolayer coverage of adsorbate, to resolve alternative geometries with the same symmetry elements (p4g) and determine atomic positions. The result of the calculations is that the nickel surface reconstructs with energy savings of about 0.4 eV and 0.3 eV for the carbon and nitrogen adsorbates respectively. The effect of the reconstruction on the electronic character of the system is examined using LCAO density of states calculations.

Interest in the effect of adsorbates on transition metal surfaces is considerable, and is stimulated by the importance of such interactions in chemical syntheses [1]. Specifically, there has been much attention paid to carbon, nitrogen and oxygen adsorbates chemisorbed onto a nickel {001} surface [2–5], with some disagreement concerning various geometries. The work presented may contribute usefully in resolving the confusion by examining the covalent energy and electronic aspects of the adsorbate–surface systems.

Extending previous work [6], this contribution examines carbon and nitrogen adsorbate interactions on a nickel (001) surface for two alternative, though very similar, geometries. The p(2 × 2) surface mesh, as opposed to a c(2 × 2) mesh, resulting from a 0.5 monolayer coverage of carbon on a nickel (001) surface is well known. The centring is removed by the surface reconstruction of the surface metal atoms, with LEED studies revealing glide lines consistent with a p4g space group [7]. There are, however, two possible adsorbate positions on the reconstructed nickel surface which would produce this symmetry. One possible geometry is for the carbon atoms to occupy a four-fold hollow site with the hollow being enlarged by a rotation and translation of surrounding nickel atoms (figure 1). An alternative position for the adsorbate is to sit in the same hollow but to pinch in two diametrically opposed surface atoms [8]. Effectively all that has changed geometrically is that the adsorbate overlayer has translated by $(0.5a, 0)$ to a position maintaining the same symmetry elements. These two geometries will be referred to as Ccs and Ccd respectively according to whether the adsorbate sits in the centre of a square or diamond formed by the surface nickel atoms.

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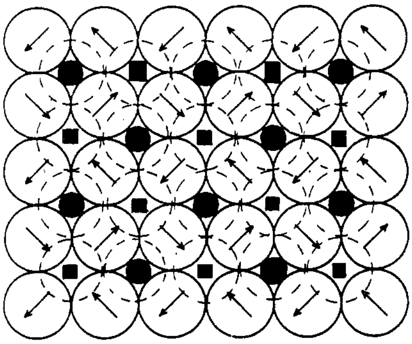

Figure 1. Symmetry for C–Ni(100) or N–Ni(001) surface. Arrows indicate direction of surface displacement. Note that the rotations for a central site are in the opposite sense compared to the four corners, thereby removing the centring of the c(2 × 2) mesh. The adsorbate sits at one of the two indicated sites for the alternate geometries (Ccs, Ccd). Large full circles, surface nickel; large broken circles, second-layer nickel; ●, adsorbate (Ccs); ■, adsorbate (Ccd).

The energy calculated is of the familiar form

$$E_{\mathrm{tot}} = E_{\mathrm{bs}} + U_{\mathrm{rep}}$$

where the total energy E_{tot} is composed of a covalent term E_{bs} and an empirical short-range repulsive term E_{rep}. The covalent term is obtained from the one-electron eigenvalues of the system and is the difference of two terms

$$E_{\mathrm{bs}} = \sum_{i_{\mathrm{occ}}} \varepsilon_i - \sum_{i_{\mathrm{occ}}} n_i e_i$$

where the first term is the sum of the occupied one-electron energy eigenvalues ε_i, and from this is subtracted the 'free atom' term, corresponding to the product of occupation of the valence orbital n_i and its energy e_i when it is a free atom.

The valence electron structure was calculated using numerical functions for the s, p and d orbitals for the metal surfaces (s and p for the adsorbates). The local density approximation was used for the exchange-correlation potential. A two-centre approximation was used to calculate the matrix element of the tight-binding Hamiltonian between orbitals on different sites, allowing a dependence only on separation and direction and ignoring the surrounding atomic environment [9]. The covalent energy was obtained by sampling a set of $\boldsymbol{k}$ points representative of the whole Brillouin zone [10].

The short-range repulsive energy U_{rep} was calculated empirically to model the repulsion felt as a result of Pauli exclusion by atoms coming close together. The two simple forms used were

$$U_{\mathrm{rep}} = \sum_{r_a} C_a \exp(-\alpha_a r_a) \qquad \text{or} \qquad U_{\mathrm{rep}} = \sum_{r_a} A_a r_a^{-12}$$

where the sums are over all near-neighbour atom pairs a at distance r_a. The form used was dependent on the empirical data available. The first form, with two fitted parameters, was used if equilibrium bond lengths and the bulk modulus were available. The second expression was used if only the interatomic distances were known. Consequently, the first form was used to model Ni–Ni repulsions with $C \simeq 282 \times 10^3$ eV and $\alpha \simeq 6.01$ Å^{-1}. The second form was used for Ni–C and Ni–N with $A \simeq 1.5 \times 10^6$ eV Å^{12} to fit equilibrium distances in bulk material. We have assumed that, as with the matrix elements, there is portability of the pairwise repulsion from bulk to surface.

The calculations were performed using a three atomic layer slab of metal with adatoms on one surface. Results from other thin slab calculations [10] suggested that

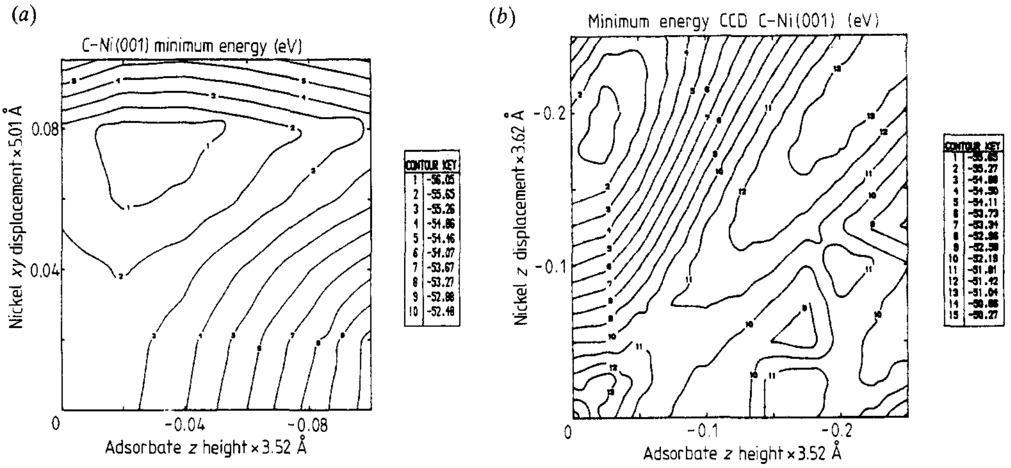

Figure 2 (*a*) Ccs. A contour plot of minimum energies for nickel *z* heights as a function of nickel transverse displacement and carbon *z* height. (*b*) Ccd. A contour plot of minimum energies for zero transverse displacement of surface nickels as a function of nickel and carbon *z* heights.

the three layers would be adequate for our purposes. The adatoms were placed in the four-fold hollow sites in what is initially a c(2 × 2) arrangement above the second-layer nickels. Each of the 12 nickel atoms in the two-dimensional slab contributes 9 orbitals, the adatoms 4, to give 116 basis functions for the k-dependent matrix, which is diagonalised to obtain the one-electron eigenvalues.

E_{tot} was then calculated for the two geometries (Ccd and Ccs) as the systems underwent a series of relaxations and surface translations with the following variable parameters;

(i) the surface metal perpendicular displacement z_{m};

(ii) the transverse displacement of the surface metal atoms x_{m} (along the [100] and [010] directions for an FCC lattice);

(iii) the adatom z displacement z_{ad}

with the second- and third-layer metal atomic positions being invariant. The energy minimum for this three-dimensional space was found and presented as energy contour plots as a function of two of the variables, at optimal values of the third variable. Figure 2(*a*) shows the most favourable nickel transverse displacement and carbon z height for optimum nickel z height. For the nickel Ccd geometry it was found that the surface metal atoms preferred not to reconstruct, and figure 2(*b*) therefore shows contours as a function of the nickel z height and carbon z height with $x_{\mathrm{n}i} = 0$. Broadly speaking, they would seem to indicate that there is an activation energy of ≃0.5–1.0 eV associated with the adsorbate moving from above the nickel to energy minima below the nickel atoms. Similar plots were obtained for nitrogen.

For the Ccs arrangement we found the adsorbate 'digging in' to the surface, forcing the surface nickel atoms aside. In both cases the adsorbate is located below the final level of the surface nickels but about 0.09 Å above the original surface nickel layer position. The calculated transverse displacement of the nickel atoms was 0.4 Å for carbon and 0.35 Å for nitrogen. At the same time the surface nickels are forced to ride

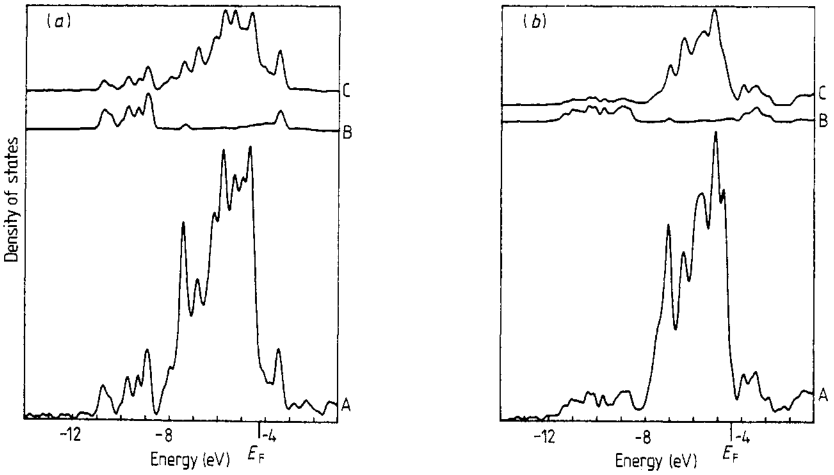

Figure 3. Calculated density of states for C–Ni(001) surface for a three-layer slab with the surface: (*a*), relaxed and unreconstructed; (*b*), reconstructed. A, total and projections onto carbon (B) and nickel (C).

up over their second-layer neighbours with a vertical displacement z_{Ni} of about 0.4 Å and 0.35 Å for carbon and nitrogen respectively. The bond lengths between the surface nickels and the two adsorbate types (C and N) were 1.88 Å and 1.84 Å respectively. The adsorbates are also coordinated with the second-layer nickels, giving bond lengths between C–N and the second-layer nickels of about 1.83 Å and 1.85 Å respectively.

The geometries of the reconstructions for the two adsorbate types are very similar but when the energies are examined the driving force for the carbon reconstruction seems to be stronger, with a binding energy per chemisorbed atom being 6.7 eV compared to 2.6 eV for nitrogen. The energy associated with the atomic rearrangements was split into two parts: the nickel–adsorbate vertical relaxation and the nickel reconstruction in the surface plane. The total energy gains for the C–Ni and N–Ni atomic rearrangements were 2.0 eV and 1.4 eV respectively. The energy saved by the latter surface reconstruction was calculated at 0.37 eV per adsorbate atom for carbon and 0.27 eV for nitrogen. Energetically, therefore, there is a greater driving force behind the carbon-induced reconstruction–relaxation than for the nitrogen.

We can examine the density of states for the relaxed but unreconstructed systems and the fully reconstructed systems to help explain the saving in band-structure energy. If we compare figure 3(*a*) for the first case for carbon and figure 3(*b*) for the reconstructed case, two differences may be noted. The coordination of the surface nickel is reduced and consequently the d bands are squeezed slightly. The principal mixing in the system is between the adsorbate p and nickel d bands and it can be seen that as the system is relaxed and reconstructed some of the upper levels within the d band drop to form a sawtooth in the DOS, providing the saving in energy. The density of states for the nitrogen adsorbate displays very similar character.

The lack of a long-range Coulomb contribution to our energy requires us to exercise caution when viewing the calculations. We are encouraged, however, by the ability of a simple calculation of the covalent aspect of bonding, such as this, to give a reasonable initial perspective of adsorbate-induced surface reconstructions. The inclusion of the Madelung energy in the near future will not only allow us to view the binding energies in a better light but also enable the investigation of systems more ionic in nature, specifically oxygen on transition metal surfaces.

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