Adsorption Site, Adsorption Energy, and Normal Vibration Frequency of H on Ni(100) via Total-Energy Calculations

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Density-functional total-energy calculations of H/Ni(100) show that the equilibrium H position is in the center site, $0.6a_0$ above the plane of the surface Ni atoms (with a Ni-H bond length of 1.8 Å). The bridge-site minimum lies only 0.1 eV higher than the center-site minimum, whereas the top-site minimum lies about 0.3 eV higher. This is consistent with a high hydrogen surface mobility.

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In recent years it has become possible to use density-functional total-energy calculations to predict a variety of properties of materials. Calculations have been performed to predict the lattice constant, cohesive energy, and bulk moduli of solids[1,2]; high-pressure phases of materials[3,4]; geometries, binding energies, and vibration frequencies of molecules[5]; surface energies[6]; and the geometry of monolayer films[7] and of surfaces.[8,9] Most total-energy calculations of surfaces have been confined to clean semiconductor surfaces, the reason being that the pseudopotential method used in these calculations is better suited to semiconductors than to transition metals, either clean or adsorbate covered. Very recently there has been some work on clean transition-metal surfaces using all-electron methods.[6,9]

In this Letter we present total-energy calculations for an adsorbate on a transition-metal surface. The particular system we have chosen is $p(1\times1)$H/Ni(100) because a variety of experiments that we can compare with have been performed on this system: thermal desorption,[10] electron energy-loss spectroscopy,[11] ion-channeling,[12] and He scattering.[13] We have performed calculations[14] to determine the geometry of the adsorbed H, its binding energy, its vibration frequency, and the barrier to surface diffusion.

Our calculations were performed using the linearized augmented plane wave method.[15,16] The core electrons (Ni $1s$-$3p$) were treated fully relativistically and the valence electrons scalar relativistically. The core is included in the calculation of the total energy and is allowed to relax from iteration to iteration (no frozen-core approximation). The potential was allowed to have a general form everywhere (no muffin-tin approximation), except that nonspherical terms within the muffin-tin spheres were evaluated approximately.[17] The non-spin-polarized form of the Vosko-Wilk-Nusair (VWN)[18] exchange-correlation potential was used. Some of the calculations were redone with use of the Hedin-Lundqvist (HL)[19] potential in order to check the sensitivity of the results to the choice of the exchange-correlation potential. Most of the calculations were performed on seven-layer slabs consisting of five layers of Ni with a layer of H on each side.

Figure 1 shows the adsorption energy $E_{\text{ads}} = (E^{\text{slab}}_{\text{H/Ni}} - E^{\text{slab}}_{\text{Ni}} - 2E^{\text{atom}}_{\text{H}})/2$ as a function of the vertical distance of the H atoms above the surface Ni plane for the center, bridge, and top sites. Here $E^{\text{slab}}_{\text{H/Ni}}$ and $E^{\text{slab}}_{\text{Ni}}$ are, respectively, the total energies (per unit cell) of the H-covered and clean Ni slabs, and $E^{\text{atom}}_{\text{H}}$ is the energy of a free spin-polarized H atom (0.957 Ry or 13.02 eV for VWN, 0.976 Ry or 13.28 eV for HL). The equilibrium position is found to be $0.6a_0$ ($a_0 = 0.529$ Å) above the center site (corresponding to a Ni-H bond length of 1.79 Å). This is probably a small

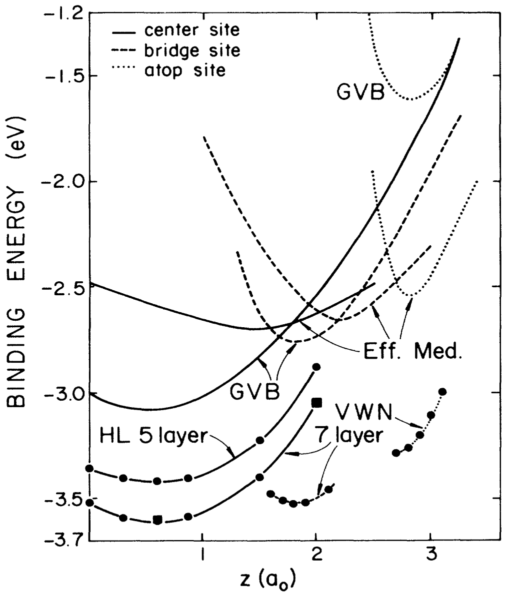

FIG. 1. Binding energy calculated by various authors as a function of the vertical distance of the H atoms above the surface Ni layer, in the center (solid curve), bridge (dashed curve), and atop (dotted curve) sites. The calculated points are generally indicated by dots. The two squares show that the results for VWN five-layer slab are similar to those for VWN seven-layer slab.

underestimate ($\approx 2\%$ or $0.07a_0$ in the bond length, or $0.31a_0$ in the vertical distance z) since local-density functional calculations for bulk Ni give a bond length that is about 2% too small. Hence, we expect the true position of the H atoms to be at about $0.9a_0$ above the surface Ni plane. Also the inclusion of magnetism (which we have neglected) would tend to increase interatomic distances slightly. In fact, a recent spin-polarized calculation[14] gives $z = 0.69a_0$. It is difficult to determine the position of H on surfaces experimentally,[20] but there is in fact a reliable determination of the position of H on Ni (100) from transmission ion-channeling experiments.[12] These experiments show that H adsorbs $(0.95 \pm 0.2)a_0$ above the center site, in excellent agreement with our estimate $(0.6+0.3)a_0$.

The calculated value of the adsorption energy (3.61 eV for VWN, 3.42 eV for HL)[21] is considerably larger than the experimental value[10] (2.7 eV). It appears to be a common failing of local-density functional theory that it gives too much binding[1,5,22] the reason being that the large underestimate of the total energies of the free atom and of the solid (4.3% for H, 0.1% for Ni) due to the local-density approximation do not quite cancel, the error being slightly larger for the atom than for the (more homogeneous) solid.

The bridge-site minimum lies only 0.08 eV higher than the center-site minimum and the top-site minimum lies about 0.32 eV higher. It ought to be mentioned here that although the individual curves have a relative numerical precision of better than 0.01 eV, there may be a relative error between the energies of the center- and bridge-site curves of 0.1 eV and of the center- and top-site curves of 0.2 eV. The reason for this is that since H atoms approach the surface Ni atoms more closely at the bridge and top sites, one is forced to choose smaller muffin-tin radii when calculating these curves, resulting in a less-well-converged basis set and greater uncertainties in the extrapolation to the infinite-basis-size energies. The extrapolation procedure is explained in greater detail later.

The near degeneracy of the center- and bridge-site minima implies that the H atoms will have large rms displacements from their equilibrium positions or may even be mobile on the surface. There is some experimental evidence that the barrier to surface diffusion of the H is small. Ion-channeling experiments[12] show that the H atoms have a rms displacement of $0.4a_0$ from their equilibrium position. Laser-induced desorption experiments[23] show that the barrier to diffusion is about 0.17 eV for H on a laser-treated Ni(100) surface. Also, H has been observed to be mobile on other transition-metal surfaces by field-ion microscopy.[24]

Also shown in Fig. 1 are other theoretical results obtained using the generalized valence bond (GVB)[25] and the effective-medium[26] methods. The inclusion of configuration effects in the GVB method restricts its application to small clusters of atoms which may not adequately represent an extended surface and may not represent the neighborhood of the center, bridge, and top sites equally well. Also, the d electrons are not included explicitly. The effective-medium technique is a simple method based on density-functional theory. It has the advantage that it is fast enough to use in complicated geometries where the more accurate methods used in our work are not feasible, and the disadvantage that it is approximate, in particular the interaction of the adsorbate with the metal d electrons is treated in a crude way. The GVB calculation gives an equilibrium position in good agreement with ours but the relative energy difference of the minima of the curves for the three sites is much larger than in our calculation. The effective-medium approach gives basically the same energy differences between the minima of the three curves as our calculation, and bond lengths that are all somewhat larger than ours. Also the detailed shape of the curves is somewhat different from ours. The semi-empirical embedded-atom method[27] gives energy differences in good agreement, and bond lengths in fair agreement with our results.

Electron energy-loss (EELS) experiments[11] for a full layer of H on Ni(100) yield a vibration frequency of 78 meV. A precise calculation of this frequency would entail a calculation of the total energy at all points in space in the neighborhood of the minimum-energy surface. Then the difference of the energies of the two lowest eigenstates for the motion of the H atom as a whole would give the EELS vibration frequency. This has been done within the effective-medium approach[28] but is difficult to do in our approach. However, an approximate estimate can be obtained from the second derivative of the energy curve near the minimum. This gives a value of 90 meV which compares reasonably well with experiment given the approximations that we have made.

Since the energies of interest are obtained by the subtraction of total energies which are several orders of magnitude larger than the energies of interest, it is important to test the convergence of our results as a function of the size of the various expansion sets used, and to test the sensitivity of our results to the choice of various parameters. Here, we discuss only some of the tests performed, namely, convergence with respect to (i) the size of the basis set used for expanding the wave functions, and (ii) the number of layers in the film, and sensitivity to the choice of the exchange-correlation potential.

One virtue of the linearized augmented plane wave method is that the basis can be systematically improved by including all plane waves with wave vectors lying within successively larger spheres of radius $K_{\max}$. Figure 2(a) shows the total energy versus the distance

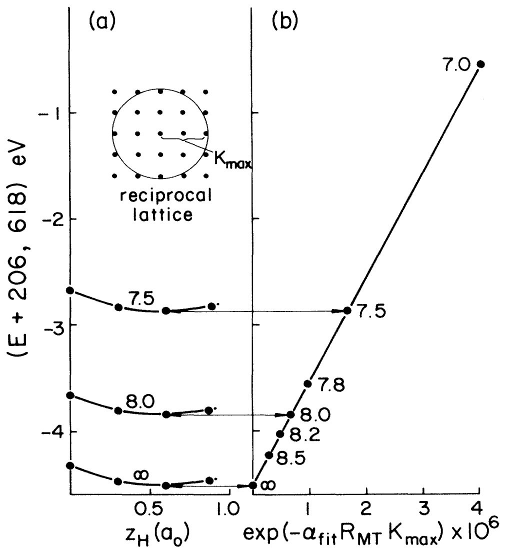

FIG. 2. Convergence of the total energy $E_{\rm tot}$ with respect to the basis size. (a) Curves of $E_{\rm tot}$ as a function of the vertical distance of the H atoms above the surface Ni layer for $R_{\rm MT}K_{\rm max}$ equal to 7.5 and 8. $R_{\rm MT}$ is the muffin-tin radius of the central-layer Ni atoms and $K_{\rm max}$ is the largest wave vector included in the basis functions. The estimated curve for an infinite basis is also shown. (b) Procedure used to estimate $E_{\rm tot}$ for an infinite basis. $\alpha_{\rm fit} = 1.78$.

of the center-site H atoms above the surface Ni layer for two values of $R_{\rm MT}K_{\rm max}$, where $R_{\rm MT}$ is the muffin-tin radius of the center-layer Ni atoms. In Fig. 2(b) the total energy for $z = 0.6a_0$ is plotted versus $\exp(-\alpha_{\rm fit}R_{\rm MT}K_{\rm max})$. The six points shown fit the exponential with an rms error of 0.008 eV. An almost equally good fit can be obtained by a power law (rms error 0.011 eV) with an exponent ≈ -12.5. The estimate of $E_{\rm tot}$ for a fully converged basis [plotted as the bottom curve in Fig. 2(a)] is obtained with assumption of the exponential dependence. Assuming the power law dependence would give a curve uniformly shifted down by 0.08 eV. The position of the minimum and the shape of the curves for $R_{\rm MT}K_{\rm max} = 7.5$ and 8.0 are almost identical. Hence it is possible to obtain the correct vertical position without having a fully converged basis as has been noticed by other authors.[7] However, since the center-, bridge-, and top-site curves are calculated with different values of the muffin-tin radii for the H and the surface Ni atoms and are therefore not equally well converged, it is very important to perform the extrapolation to obtain the relative energy differences between them.

The binding energies of H at two positions above the center site were recalculated with use of a thinner slab consisting of three Ni layers with a layer of H on each side (shown as square data points in Fig. 1). The close agreement between these energies and those for the fatter slab gives us confidence that the energies are converged with respect to the thickness of the slab.[29]

Figure 1 also shows that use of the HL exchange-correlation potential instead of the VWN potential results in a binding-energy curve almost parallel to that for the VWN potential over the range of distances shown, but shifted up by 0.19 eV.

We have shown that accurate total-energy calculations can be used to determine the geometry of adsorbates on surfaces.

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[21] For the expert, the small difference between our adsorption energy (3.42 eV) and that of Weinert and Davenport (3.24 eV) can be reconciled by the following equation:

$$3.42[E_{\mathrm{coh}}^{\mathrm{UW}}]-0.11[E_{\mathrm{Ni}}^{\mathrm{WD}}(\mathrm{mag})-E_{\mathrm{Ni}}^{\mathrm{UW}}(\mathrm{nonmag})]$$
$$+0.00[-E_{\mathrm{H/Ni}}^{\mathrm{WD}}(\mathrm{mag})+E_{\mathrm{H/Ni}}^{\mathrm{UW}}(\mathrm{nonmag})]$$
$$-0.04[\mathrm{H\ zero\text{-}point\ energy}]\approx 3.24[E_{\mathrm{coh}}^{\mathrm{WD}}].$$

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