

micelle size in the critical region is not considerably dependent on T , as found in a recent neutron-scattering experiment on C_8Et_4 solutions.²

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Calculated Binding Properties of Hydrogen on Nickel Surfaces

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An extremely simple calculational method based on the effective medium theory is developed to describe chemisorption systems. It is tested for hydrogen chemisorbed on Ni(100) and (111). Good agreement with experiment is obtained for all quantities calculated: chemisorption energy, equilibrium position, vibrational frequency, and the energy of the hydrogen-induced level. The results indicate that hydrogen may exist under the first Ni layer of Ni(111), but that the binding here is weaker than outside the surface.

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In the present Letter, an extremely simple calculational method is presented which allows the calculation of the full potential-energy surface for an atom interacting with a metal surface. The method is tested for the H/Ni(100) and H/Ni(111) chemisorption systems. Contrary to the proposal of Eberhard, Greuter, and Plummer¹ the results do not show hydrogen under the Ni(111) surface to be more stable than on the surface, but it is suggested that at low temperature both sites can be filled. This can explain both the photoemission¹⁻³ and the low-energy electron diffraction⁴ results, as well as the two peaks observed in electron energy-loss spectroscopy.⁵ Similar good agreement with experiment is found for H/Ni(100).

The calculational scheme used is a new version

of the effective medium theory.^{6,7} The binding energy of an atom (hydrogen) to a host (nickel surface) is written⁷

$$\Delta E = \Delta E^{\text{hom}}(\bar{n}_0) - \alpha_{\text{at}} \bar{n}_0 + \delta \int_{-\infty}^{\epsilon_F} \Delta n(\epsilon) \epsilon d\epsilon. \quad (1)$$

For a full derivation of Eq. (1) the reader is referred to Ref. 7. The starting point is the hydrogen atom in a homogeneous electron gas (the effective medium). ΔE^{hom} is the binding energy here. The electron-gas density \bar{n}_0 is chosen as an average of the host electron density $n_0(\vec{r})$ over the atom electrostatic potential.^{6,7} The second term is an electrostatic term which has been expressed⁷ as a constant α_{at} , only depending on the atom in question, times \bar{n}_0 . The third term is the difference in the sum of the one-electron energies of the atom-induced states [density of

states $\Delta n(\epsilon)$] between the homogeneous effective medium and the real host. Within the local density approximation,⁸ the expression Eq. (1) is exact to first order in a mixed perturbation theory where the difference of $n_0(\vec{r})$ from homogeneity is treated to first order in the region close to the atom, where the atomic potential dominates, and the atom-induced density is treated to first order in the region outside, where the host dominates.

In Ref. 7 the theory was used to calculate the hydrogen heats of solution in the $3d$ transition metals. It was argued that in these cases there are two main contributions to the one-electron term in Eq. (1): (1) the first-order change $\int [n_0(\vec{r}) - \bar{n}_0] \Delta V_{\text{eff}}(\vec{r}) d^3r$ in the one-electron energies due to the atom-induced potential ΔV_{eff} , and (2) the hybridization of the hydrogen-inhomogeneous-electron-gas state with the metal d band. The former can be shown numerically to scale roughly with \bar{n}_0 .⁷ In treating (2), it is worth noting that in the homogeneous electron gas, the hydrogen-induced state is situated just below the electron-gas effective potential V_{eff}^0 at all metallic densities. When the hydrogen atom is moved from the electron gas to the real host the value of V_{eff}^0 at the hydrogen site is the common ener-

gy zero.⁷ Since V_{eff}^0 is much lower than the center of the d band, C_d , and $C_d - V_{\text{eff}}^0$ is large compared to the d -band width, the hybridization can be treated to lowest order in the $3d$ -hydrogen overlap V_{ad} . Under these assumptions the hydrogen binding energy can be written⁷

$$\Delta E = \Delta E^{\text{hom}}(\bar{n}_0) - \alpha_{\text{eff}} \bar{n}_0 - 2(1-f)N_d \frac{|V_{\text{ad}}|^2}{C_d - V_{\text{eff}}^0}. \quad (2)$$

Here N_d is the effective number of d states interacting with the hydrogen atom and f is the degree of filling of the d band. The $1-f$ factor thus represents the competition between the bonding and antibonding contributions to the hybridization energy ΔE^{hyb} . The factor of 2 comes from spin (magnetic effects are neglected).

The properties of the hydrogen atom enter Eq. (2) through ΔE^{hom} , α_{eff} , the sampling function in \bar{n}_0 , and the fact that the hydrogen level is located at V_{eff}^0 before hybridization with the d band. For the sampling function the free-atom electrostatic potential can be used.⁷ ΔE^{hom} and α_{eff} can be calculated once and for all.^{6,7} A parametrized form of the two first terms in Eq. (2) is (n_0 in a_0^{-3})

$$\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0) = \Delta E^{\text{hom}}(\bar{n}_0) - \alpha_{\text{eff}} \bar{n}_0 = \begin{cases} 130\bar{n}_0 \ln(\bar{n}_0/0.004) - 252\bar{n}_0 - 1.12 \text{ (eV)}, & 0.002 < n_0 \leq 0.0127; \\ 398(\bar{n}_0 - 0.0127)^2 + 31\bar{n}_0 - 2.81 \text{ (eV)}, & 0.0127 \leq n_0. \end{cases} \quad (3)$$

The properties of the host enter Eq. (2) through $n_0(\vec{r})$, V_{eff}^0 , and the d -band parameters C_d and f . The latter three are tabulated (see Ref. 7). For $n_0(\vec{r})$ a superposition of atomic charge densities are used. By direct comparison to self-consistent calculations it has been demonstrated that at the open sites considered here this gives an error of less than 10%.⁹

Finally $N_d |V_{\text{ad}}|^2$ is a parameter which cannot be determined independently. Under the assumption that it is constant and of a value that gives a good overall agreement in the absolute values, all the trends in the hydrogen heats of solution in the $3d$ (and 4 and $5d$) series can be accounted for.⁷ A point to note is that $\Delta E_{\text{eff}}^{\text{hom}}$ gives the bulk of the binding energy so that the more crudely described hybridization term has a relatively small importance.

By extending the use of Eq. (2) to the chemisorption problem, a superposition of atomic charge densities is still used for $n_0(\vec{r})$. This works as

well (or even better) as in the bulk.⁹ The effective potential $V_{\text{eff}}^0(\vec{r})$ at the hydrogen position \vec{r} is calculated from $n_0(\vec{r})$. The only new feature is that a position dependence must be given to the parameter $N_d |V_{\text{ad}}|^2$. This is done by writing

$$N_d |V_{\text{ad}}(\vec{r})|^2 = \sum_{\vec{R}} N_d^{\text{at}} |V_{\text{ad}}^{\text{at}}(|\vec{r} - \vec{R}|)|^2,$$

where $V_{\text{ad}}^{\text{at}}$ is taken to scale with distance $|\vec{r} - \vec{R}|$ to the Ni atoms as the atomic-metal- $3d$ -hydrogen- $1s$ overlap integral. N_d^{at} is constant for all the Ni atoms and so at symmetrical hydrogen sites $N_d |V_{\text{ad}}(\vec{r})|^2$ scales with the coordination number.

The scaling with the overlap integral is a reasonable assumption but it is clearly the weakest point in the calculation. Again, however, it must be kept in mind that the hybridization term is only a small fraction of the binding energy. For H on Ni(111) at the equilibrium site \vec{r}_{eq} , $\Delta E(\vec{r}_{\text{eq}}) = -2.70$ eV whereas $\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0(\vec{r}_{\text{eq}})) = -2.45$ eV.

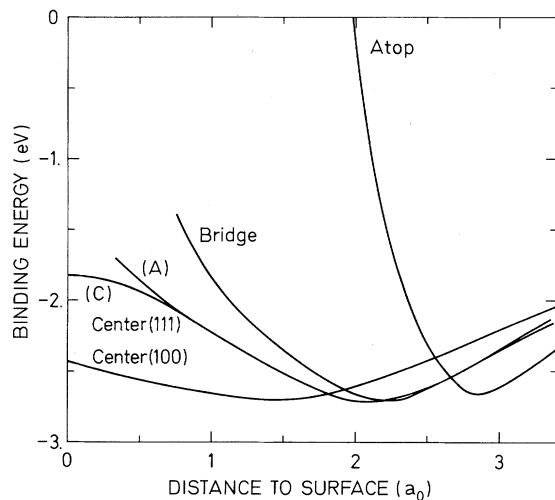


FIG. 1. Binding energy of H as a function of distance outside the atop, bridge, and center sites on the Ni (100) and (111) surfaces. The atop and bridge sites are indistinguishable for the two surfaces. For the (111) surface, the difference between center sites with and without an atom underneath [center (A) and center (C), respectively] only shows up very close to the surface. The distance is relative to the first Ni layer.

The absolute value of $N_d |V_{ad}|^2$ is chosen so that Eq. (2) reproduces the observed bulk heat of solution of the metal in question.¹⁰

In Fig. 1 examples of calculated potential energy curves for H outside the atop (A), bridge (B), and center (C) sites of Ni(100) and (111) are

shown. For both surfaces the B and C sites are slightly more stable than the A site. When the zero-point motion is taken into account the C site is most stable (by ~ 0.05 eV relative to B) whereas A is higher in energy than C by 0.15 eV. The small energy differences may be due to the pair structure of V_{ad} . The other extreme, where the d electrons are assumed totally delocalized so that V_{ad} varies with distance from the surface only, would increase these differences. The small C-B difference indicating a tendency for hydrogen to delocalize is, however, in good agreement with the low-energy electron diffraction observations.^{4,11}

Qualitatively the results of Fig. 1 agree well with those of quite different theoretical approaches ranging from Hückel¹² to Hartree-Fock cluster calculations.¹³

The equilibrium properties of hydrogen on Ni(100), Ni(111), and in the subsurface layer of Ni(111) are summarized in Table I. Notice that whereas it is easy to relax the first Ni layer in the subsurface calculation, the restoring Ni-Ni interactions are not included in the present work. The equilibrium relaxation can therefore not be determined. With no relaxation the subsurface binding energy is basically equal to that in the bulk. Relaxing the first layer decreases ΔE , but it never gets as low as outside the surface even without the restoring forces. The surface relaxation is closely related to the expansion of the Ni

TABLE I. Equilibrium properties of H on the Ni (100) and (111) surfaces and between the first and second layer on Ni (111). Site, Ni-H distance ($d_{\text{Ni-H}}$), binding energy (relative to the free atom, the surface zero-point energy is not included) (ΔE), vibrational frequency (ω_0), and position of the hydrogen level with respect to the Fermi level (ϵ_b) are shown. For H under the first layer ΔE can only be estimated because the Ni-Ni interactions are not included (see text). The experimental results are placed to give the best agreement with theory. This involves new assignments of sites (see text).

Surface	Site	$d_{\text{Ni-H}}$ (a_0)	ΔE (eV)	ω_0 (meV)	ϵ_b (eV)
Ni (100)	Theory C	3.63	-2.7	79	-5.7
	Expt. C ^a	...	-2.74 ^d	74 ^a	...
Ni (111)	Theory C	3.44	-2.7	134	-5.7
	Expt. C ^b	3.47 ^b	-2.74 ^d	139 ^e	-5.9 ^f
Ni (111) subsurface	Theory oct.	3.53 ^c	~ -2.5	83	-8.2
	Expt.	79 ^e	-7.5 ^g

^aReference 11.

^bReference 4.

^cReference 14.

^dReference 15.

^eReference 5.

^fReference 2.

^gReference 1.

lattice when forming the bulk hydride. In Table I the hydride Ni-H distance has therefore been chosen as representative of that of the subsurface hydrogen. Independent of this, it can be concluded that the present calculations do not support a picture where the subsurface hydrogen is the most stable. Instead they suggest the most stable position to be outside the surface, but that, at low temperature, more hydrogen can be accommodated under the surface. When the sample is heated up, the subsurface hydrogen either desorbs or moves to empty surface sites. This interpretation has first been proposed for the similar H/Pt case by Kasemo.¹⁶ It gets support from the observation that polycrystalline Ni adsorbs about 40% more hydrogen at 100 K than at room temperature.¹⁷ With this interpretation all of the observed properties of the H/Ni(111) system can be understood as indicated in Table I. The high-frequency electron energy-loss peak thus corresponds to the surface perpendicular mode, whereas the low-frequency peak is due to the subsurface hydrogen. The potential parallel to the surface is so soft towards the B site that the parallel mode will have an extremely low frequency. The hydrogen level positions quoted in Table I are simply estimated from the value of $V_{\text{eff}}^0(\vec{r})$ at the hydrogen site \vec{r} and a hybridization shift

$$\frac{N_d |V_{\text{ad}}(\vec{r})|^2}{C_d - V_{\text{eff}}^0(\vec{r})} \simeq -1 \text{ eV.}$$

These estimates agree well with the theory of Muscat and Newns.³

The new interpretation suggested here may, of course, not be the only one possible. H-H interactions, which are not included here, could, for instance, be important. The above does, however, indicate the usefulness of a theory simple enough to provide an interplay with experiment.

The simple division of ΔE [Eq. (2)] into $\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0)$ and ΔE^{hyb} can also be used to obtain a new picture of the hydrogen chemisorption bond. $\Delta E_{\text{eff}}^{\text{hom}}$ or the homogeneous-electron-gas part of the binding energy describes mainly the interaction with the surface s - p electrons. Outside a surface, the optimum density ($\bar{n}_0 \sim 0.01a_0^{-3}$), where $\Delta E_{\text{eff}}^{\text{hom}}$ [Eq. (3)] takes its minimum value of -2.45 eV, can always be found. $\Delta E_{\text{eff}}^{\text{hom}}$ therefore contributes the same to the chemisorption energy at any surface. The (small) differences between different metals, different surfaces, or different sites are thus due to ΔE^{hyb} .

The hybridization term ΔE^{hyb} is relatively small simply because the interaction of the hydro-

gen $1s$ level with the surface s - p electrons has already shifted it away in energy from the d band. When the hydrogen atom is moved away from the surface, $C_d - V_{\text{eff}}^0$ and V_{ad} decrease simultaneously.¹⁸ This means that the distance variation of ΔE^{hyb} is much weaker than for $\Delta E_{\text{eff}}^{\text{hom}}$. The equilibrium distances perpendicular to the surface and the vibrational frequencies are thus determined by $\Delta E_{\text{eff}}^{\text{hom}}$.

As mentioned above, the trends in the chemisorption energies along, e.g., the $3d$ series will be given by the hybridization term. This has been calculated in Ref. 7 (Fig. 5). The result is in good general agreement with experiment¹⁹ and with the results of Muscat and Newns.³ Indeed, their embedded cluster method can be regarded as a more detailed way of calculating the one-electron term in Eq. (1). Generalizing, the present picture provides a way of explaining why one-electron-energy changes are often found to give a good qualitative description of bonding in both chemisorption²⁰ and other chemical systems.

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