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Effective medium potentials for molecule–surface interactions: H₂ on Cu and Ni surfaces

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A new approximate method is developed for the calculation of the adiabatic potential energy surface for a molecule outside a metal surface. It is computationally fast enough to be useful in simulations of the dynamics of adsorbing and desorbing molecules. The method is characterized by the fact that the functional form of the total energy expression is derived from density functional theory, that each of the terms entering can be given a precise physical interpretation, and that most of the parameters entering can be calculated, within the local density approximation. The method is explicitly derived for H₂ outside metal surfaces and the applicability is illustrated for H₂ adsorbing on various Cu and Ni surfaces. Although very approximate, the calculated potentials seem to include a number of features observed experimentally: Ni is more active in dissociating H₂ than Cu, and open surfaces are more active than close-packed ones. Moreover, the method is simple enough that one can contemplate studying variations in dissociation pathways over the surface unit cell. For the Cu surfaces these variations are substantial accounting for at least part of the variation of the sticking coefficient with the kinetic energy of the incoming molecule. Because of the transparent nature of the energy expression, all these trends can be given a simple physical interpretation.

I. INTRODUCTION

A theoretical treatment of chemisorption, dissociation, or sticking of molecules on metal surfaces usually consists of three components: (i) a calculation of the adiabatic potential energy surface; (ii) a simulation of the dynamics in this potential; and, sometimes, (iii) an inclusion of nonadiabatic effects on the dynamics.

The present paper addresses point (i), the calculation of the potential. The simplest approach is to assume some simple form for the interatomic interactions like pair potentials and then fit the parameters to experiments. This has the computational simplicity needed in dynamics simulations, where the energy or the forces have to be calculated continuously, but may not provide a good enough representation of the true many body interactions in the system.

Large scale *ab initio* calculations of molecule–surface interaction potentials are still scarce. A system with a molecule outside a surface has so low symmetry that the electronic structure problem becomes enormous. In all calculations up till now the surface has been modeled by a simpler substrate, jellium^{1–3} or a small cluster.^{4–7} Even these calculations are, however, far too time consuming to be of general use in simulating reaction dynamics.

It is the purpose of the present paper to introduce a new method for calculating molecule–surface interaction energies which is computationally simple enough to be of use in dynamics simulations, but has some of the advantages of the *ab initio* methods: the functional form is derived from density functional theory and the parameters entering can, for the most part, be derived from independent calculations. The method is based on the effective medium theory,⁸ which has proven able to give a good description of static properties of bulk metals⁸ and of metal surfaces, including surface energies,⁸ surface relaxations, chemisorption on metal sur-

faces.^{10,11} Furthermore, it has been used in Monte Carlo simulations of the thermal expansion of bulk metals¹² and in a molecular dynamics simulation of the melting of metal surfaces.¹³

Two earlier attempts have been made to extend effective medium theory or related methods to treat molecules outside surfaces.^{14,15} They both fit to make sure that the free molecule is well described, but do not take into account that the molecular bond completely changes character during the adsorption process. Model calculations for H₂ inside and adsorbed on jellium surfaces point to the importance of the antibonding molecular level being filled during the adsorption and dissociation process.^{1–3,16} In the present approach, an attempt is made to incorporate these effects. The functional form derived for the interaction energies is still used, but in calculating some of the parameters it has been necessary to lean heavily on the above mentioned model calculations.

The applicability of the approach is illustrated by calculations of the total energy of an H₂ molecule outside various Cu and Ni surfaces. In spite of the approximate nature of the theory, the results appear in reasonable agreement with known experimental data on these systems.^{17–20} It allows for the first time an estimate of the variations of the dissociation pathways along the surface unit cell. It also provides a clear physical picture of the dissociation process and of the difference between H₂ dissociation on Cu and Ni. The application of the potential for dynamics simulations will be described in a future publication.²¹

The paper is organized as follows. First the basic notions of effective medium theory are summarized. Then the extension to the molecular problem is discussed in Sec. III, with special emphasis on H₂. In Sec. IV the results for H₂ outside Cu and Ni are presented, and finally, in Sec. V, the main conclusions are summarized.

II. EFFECTIVE MEDIUM THEORY

The basic idea in the effective medium theory is the following. Consider an atom i which is part of a larger condensed system of atoms. Atom i can be considered embedded in the (inhomogeneous) electron gas setup by the surrounding atoms. As a starting point we can calculate the effect of the surroundings on the energy of atom i by considering the average effect. That is, instead of calculating the energy of atom i in the real host setup by the surrounding atoms we do the calculation as if it was embedded in a homogeneous electron gas (the effective medium) of a density given by the average electron density from the surroundings. The total binding energy of the system is then given by

$$E_{\text{tot}} = \sum_i E_{\text{hom},i}(\bar{n}_i) + \text{corrections}, \quad (1)$$

where $\Delta E_{\text{hom},i}(n)$ is the energy of embedding atom i in a homogeneous electron gas (jellium) of density n . The corrections are due to the nonhomogeneity of the real system.

This approach can be formalized within the density functional formalism by assuming that the total electron density of the system can be written

$$n(\mathbf{r}) = \sum_i \Delta n_i(|\mathbf{r} - \mathbf{R}_i|), \quad (2)$$

where $\Delta n_i(r)$ is the density of atom i when embedded in a homogeneous electron gas of a density given by an average (to be defined in more detail later) of the tails from the neighbors. Within the local density approximation for exchange and correlation effects this density gives a total binding energy which can be written on the form of Eq. (1)⁸:

$$E_{\text{tot}} = \sum_i \Delta E_{\text{hom},i} + E_{\text{es}} + \Delta E_{\text{xc}} + E_{\text{kin}}. \quad (3)$$

Due to the variational property of the total energy functional, expression (3) only has errors which are second order in the difference between the ansatz density Eq. (2) and the true ground state electron density of the system. Furthermore, Eq. (3) has been derived including the difference between the tail densities from the surroundings around a given atom i and their average \bar{n}_i only to the first order. Again the variational principles ensures that this only gives rise to second order errors in the total energy. The correction terms in Eq. (3) are within the local density approximation.

$$E_{\text{es}} = \frac{1}{2} \sum_{(ij)} \iint \frac{\Delta \rho_i(\mathbf{r}') \Delta \rho_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (4)$$

$$\Delta E_{\text{xc}} = \int \left\{ f_{\text{xc}}[n(\mathbf{r})] - \sum_i \left[f_{\text{xc}}(\bar{n}_i + \Delta n_i(\mathbf{r})) - f_{\text{xc}}[\bar{n}_i(\mathbf{r})] \right] \right\} d\mathbf{r}, \quad (5)$$

$$\Delta E_{\text{kin}} = \int \left(t - \sum_i \Delta t_i \right) d\mathbf{r}. \quad (6)$$

Here, $f_{\text{xc}}(n) = e_{\text{xc}}(n)n$ is given by the exchange correlation energy density e_{xc} , and t and Δt_i are the kinetic energy densities for the full system and for the atom in the homogeneous electron gas, respectively. For a full derivation the reader is referred to Ref. 8.

For a close packed (FCC or HCP) metal, Eq. (3) can be considerably simplified by dividing space into Wigner-Seitz cells—or, to a good approximation—Wigner-Seitz spheres s_i . Then

$$E_{\text{tot}} = \sum E_{c,i} + \Delta E_{\text{1el}}, \quad (7)$$

where

$$E_{c,i} = \Delta E_{\text{hom},i} - \alpha_i \bar{n}_i, \quad (8)$$

$$\alpha_i = \int_{s_i} \Delta \phi(\mathbf{r}) d\mathbf{r}, \quad (9)$$

and

$$\Delta E_{\text{1el}} = \int_{-\infty}^{\epsilon_F} \Delta n_i(\epsilon) \epsilon d\epsilon - \int_{-\infty}^{\bar{\epsilon}_F} \Delta \bar{n}_i(\epsilon) \epsilon d\epsilon. \quad (10)$$

$\Delta n_i(\epsilon)$ and $\Delta \bar{n}_i(\epsilon)$ are the local atom i -induced density of states in the real and effective host, respectively. In this case the density \bar{n}_i is naturally defined as the average of the tails from the surroundings over the volume s_i .

The $E_{c,i}$ function contains all the explicit \bar{n}_i dependence. It can be calculated once and for all within the local density approximation.⁸ Some examples are shown in Fig. 1. All atoms except the rare gasses show a single minimum in $E_{c,i}(n)$. The minimum is a result of a competition between the kinetic energy repulsion which dominates $\Delta E_{\text{hom},i}(n)$ at large n and the second term on the right-hand side of Eq. (8), which represents the electrostatic attraction between the surrounding electrons and the electrostatic potential due to atom i .

The one-electron energy difference ΔE_{1el} is important in cases where the integrated one-electron spectrum looks different in the real host compared to the atom in a homogeneous electron gas. As discussed in Ref. 8 this term is unimportant for the simple and noble metals, whereas for the transition metals it includes the effects of d -band broadening.

For metals where $\Delta E_{\text{1el}} \approx 0$ the depth of the minimum in E_c gives the cohesive energy, the curvature gives the bulk modulus, and the position of the minimum gives directly the

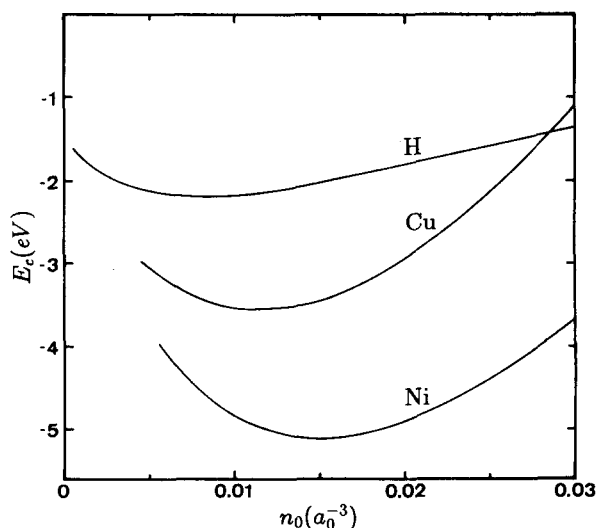


FIG. 1. The E_c functions for H, Cu, and Ni. From Ref. 8.

TABLE I. Comparison of calculated properties of bulk metals to the results from the calculation of Morruzi, Janak, and Williams (Ref. 36) and to experiment (Refs. 36 and 37). The d - d coupling has been neglected for Ni.

	Cu			Ni		
	EMT	MJW	Exp.	EMT	MJW	Exp.
$R_{ws} (a_0)$	2.58	2.64	2.67	2.46	2.56	2.60
$E_{coh} (eV)$	-3.56	-4.08	-3.52	-5.12	-5.62	-4.39
$B(\text{Mbar})$	1.85	1.55	1.37	3.09	2.20	1.86

equilibrium lattice constant. Values extracted from the results of Fig. 1 are shown in Table I where they are compared to results from experiment and from much more involved calculations.

For nonclose packed systems—non-fcc structures, phonons, disordered systems, surfaces, and for atomic impurities inside and outside metals we choose to still to work with neutral atomic spheres, so that the two terms in Eq. (7) remain unchanged, but then we have to correct for the fact that part of space have not been included at all whereas other parts are counted twice due to overlap between spheres. This is completely dominated by the electrostatics, and is included as the atomic sphere correction

$$\Delta E_{AS} = -\frac{1}{2} \int O(\mathbf{r})\rho(\mathbf{r})\phi(\mathbf{r}) \quad (11)$$

where the overlap function $O(\mathbf{r})$ is defined to be $n-1$ if \mathbf{r} is in n of the atomic spheres ($n = 0, 1, 2, \dots$). $\rho(\mathbf{r})$ and $\phi(\mathbf{r})$ are the total charge density and electrostatic potential, respectively.

Contributions to ΔE_{AS} from two atoms of the same kind can be expressed analytically in terms of the densities.⁸ For adsorbates on surfaces we have calculated Eq. (11) directly by noting that the integrand is largest in the overlap region ($O \gg 1$). The contribution to the atomic sphere correction energy from an adsorbate and a metal atom is therefore approximated by the overlap contribution^{10,11}

$$\Delta E_{AS}^{MA} = -\frac{1}{2} \int_{s_M \cap s_A} [\Delta n_M(\mathbf{r})\Delta\phi_A(\mathbf{r}) + \Delta\phi_M(\mathbf{r})\Delta n_A(\mathbf{r})] d\mathbf{r}. \quad (12)$$

This approach gives a good description of bulk phonons,⁸ the thermal expansion,¹² surface energies,⁸ surface relaxations,⁸ surface reconstructions,⁹ and of the premelting process.¹³ Of particular interest here is the fact that it also gives a reasonable account of hydrogen chemisorption on metal surfaces. This is illustrated in Table II, where calculated and measured properties of hydrogen chemisorbed on Cu(100) and Ni(100) are compared. In addition, the theory can describe subtle effects like the hydrogen-induced changes in interlayer spacings.¹⁰

In Fig. 2 we show the various contributions to the hydrogen chemisorption energy outside the fourfold center site on Cu(100). It is seen that the binding energy, the vibrational frequency and the equilibrium position are all dominated by the E_c function.³²

TABLE II. Comparison of calculated and experimentally measured properties of atomic hydrogen on Cu and Ni surfaces. The experimental results are from Refs. 18, 29, 38, and 39. For Ni the adsorbate-metal d coupling parameter is chosen to be $M/M_H = 0.75$ (cf. Table IV).

	H/Cu(100)		H/Ni(100)	
	EMT	Exp.	EMT	Exp.
$d_{M-H} \text{(\AA)}$	2.01		1.87	1.83
$E_{chem} (eV)$	-2.40	-2.40	-2.66	-2.63
$\omega (meV)$	75		78	74

III. H₂ ADSORPTION ON METAL SURFACES

As mentioned in the Introduction we shall be centering the present discussion around the hydrogen molecule. There are, in principle, no limitations in this respect, however. Before considering the molecule outside the surface, we start by looking at the free H₂ molecule.

A. The free molecule

The most naive application of the effective medium concept to the treatment of a diatomic molecule would be to simply say that the binding energy is $E_B(R) = 2E_c[\Delta n_H(R)]$, where $\Delta n_H(R)$ is the hydrogen (in jellium) density, and R is the internuclear separation. This does not give a too bad representation of the 'exact' local density calculation of Johansson and Gunnarsson²³ as can be seen in Fig. 3. The correction

$$\delta(R) = E_{H_2}^{exact} - 2E_c[\Delta n_H(R)] \quad (13)$$

is seen to be a smooth function, which is attractive for small distances, but becomes positive at large distances.

In the following we shall derive the correction terms that make up $\delta(R)$ and show that a direct evaluation of them gives values of the correct order of magnitude. For the rest of the paper we will, however, simply use the $\delta(r)$ defined in Eq. (13), with appropriate modifications when the molecule

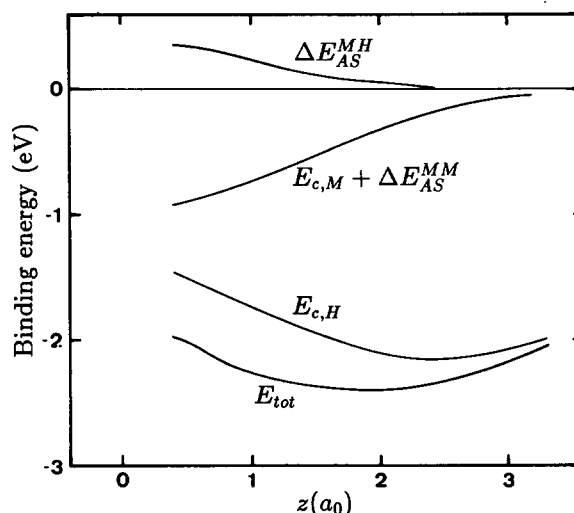


FIG. 2. The different contributions Eqs. (7)–(12) to the chemisorption energy for hydrogen outside the center site on Cu(100).

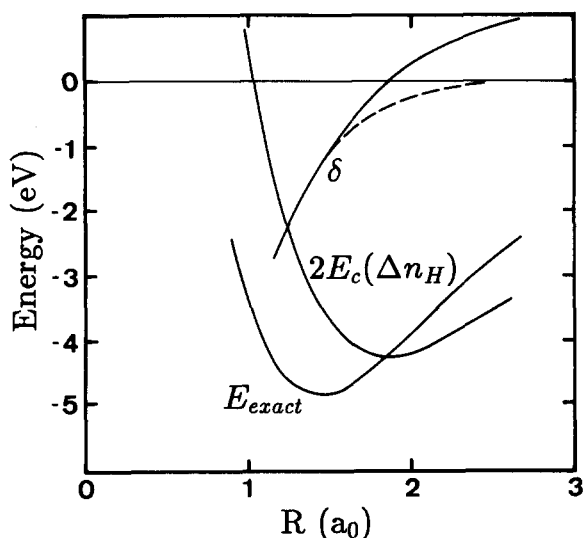


FIG. 3. The exact results from Gunnarsson and Johansson (Ref. 23) compared to the simplest effective medium theory estimate and the difference δ between the two.

interacts with a metallic system. The discussion of these modifications is the subject of the next subsection.

When considering a diatomic molecule it is no longer natural to divide space up into neutral overlapping spheres and then consider the corrections afterwards. Instead we simply divide space up into two half-spaces by the molecular mirror plane. We then go back to the expression Eq. (3), and consider the correction terms one by one.

Simple rearrangements of Eq. (4) give

$$E_{es} = 2 \int_1 [\Delta\rho_2(\mathbf{r}) - \bar{n}_1] \Delta\phi_1(\mathbf{r}) d\mathbf{r} - 2\alpha\bar{n}. \quad (14)$$

Here we have explicitly used that the two atoms are equivalent (the factor of 2). The α is defined as in Eq. (9) except the integral is over the half-space 1 (or 2). This does not, however, make a noticeable difference in the magnitude. The average density from one hydrogen atom around the other we take as the value at the nucleus. Again it makes very little difference exactly how this is done and we shall not at this level of accuracy pursue this issue further.

The exchange-correlation energy difference Eq. (5) can be written

$$\begin{aligned} \Delta E_{xc} &= 2 \left\{ \int_1 f_{xc} [\Delta n_2(\mathbf{r})] \right. \\ &\quad \left. - \int_2 [f_{xc} (\Delta n_1(\mathbf{r}) + \bar{n}_1) - f_{xc} (\bar{n}_1)] d\mathbf{r} \right\} \\ &= \Delta E_{xc}^{\text{tail}} + \int_1 \Delta v_{xc}(\mathbf{r}) [\Delta n_2(\mathbf{r}) - \bar{n}_1]. \end{aligned} \quad (15)$$

The exchange-correlation potential in Eq. (15) is given by $\Delta v_{xc} = v_{xc}(\Delta n_1 + \bar{n}_1) - v_{xc}(\bar{n})$. This means that

$$\begin{aligned} E_{es} + \Delta E_{xc} &= 2 \left\{ \int \Delta v_1(\mathbf{r}) [\Delta n_2(\mathbf{r}) \right. \\ &\quad \left. - \bar{n}_1] d\mathbf{r} - \alpha\bar{n} \right\} + \Delta E_{xc}^{\text{tail}}. \end{aligned} \quad (16)$$

The kinetic energy part Eq. (6) can be written

$$\begin{aligned} \Delta E_{\text{kin}} &= \int_{-\infty}^{\epsilon_F} n(\epsilon) \epsilon d\epsilon - \int_{-\infty}^{\bar{\epsilon}_F} 2\Delta\bar{n}(\epsilon) \epsilon d\epsilon \\ &\quad - 2 \left\{ \int_1 [\Delta n_2(\mathbf{r}) - \bar{n}_1] \Delta v_1(\mathbf{r}) d\mathbf{r} \right. \\ &\quad \left. - \int_2 \Delta v_1(\mathbf{r}) [\Delta n_1(\mathbf{r}) + \bar{n}_1] \right\}. \end{aligned} \quad (17)$$

Collecting Eqs. (16) and (17) and using the definition Eq. (8) for E_c we get

$$\begin{aligned} \Delta E_{\text{tot}} &= 2E_c(\bar{n}) + \int_{-\infty}^{\epsilon_F} n(\epsilon) \epsilon d\epsilon - \int_{-\infty}^{\bar{\epsilon}_F} 2\Delta\bar{n}(\epsilon) \epsilon d\epsilon \\ &\quad + 2 \int_2 \Delta v_1(\mathbf{r}) [\Delta n_1(\mathbf{r}) + \bar{n}_1] + \Delta E_{xc}^{\text{tail}}. \end{aligned} \quad (18)$$

The three last terms in Eq. (18) (counting the one-electron energy difference as one term) thus represent the effective medium theory approximation to $\delta(r)$ defined above. At $R = 1.4$ a.u., the H_2 equilibrium internuclear distance, δ from Fig. 2 is -1.51 eV. The three last terms in Eq. (18) are, respectively, $+0.68$, -2.76 , and $+0.72$ eV, summing up to -1.36 eV. The one-electron energy difference has been estimated in the following way: The one-electron spectrum of hydrogen embedded in a homogeneous electron gas is sketched in Fig. 4.¹⁶ It consists of a doubly occupied bound state just below the bottom of the band and an antiresonance (the screening electrons) just above. The sum of one electron energies is thus very close to the value of the bottom of the band. When the potentials in the different cells are lined up this must be made so that the "local bottom of the band" is⁸

$$v^0 = \phi(R) + v_{xc} [\Delta n_H(R)]. \quad (19)$$

The one-electron energy difference is then estimated as $2(\epsilon_\sigma - v^0)$ where ϵ_σ is the energy of the bonding level for H_2 taken from an independent calculation for the free H_2 molecule.¹⁶ Figure 4 also shows why this term is so relatively small. The hydrogen state in the homogeneous electron gas has had a bonding shift due to the interaction with the electron gas states, which is comparable to the one the hydrogen states get in H_2 .

The behavior of $\delta(R)$ at large R has a completely different origin. It is related to a general problem in the effective medium theory. The E_c or ΔE^{hom} functions are defined as

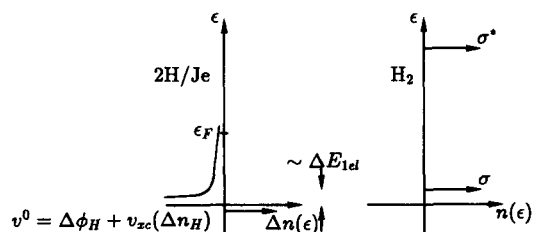


FIG. 4. Schematic picture of the one-electron spectrum for a H atom in a homogeneous electron gas compared to that of the diatomic molecule. The one-electron energy difference in Eq. (18) is the difference between the first moment up to the Fermi level of the H-in-jellium density of states (which is approximately equal to the value v^0 of the bottom of the band) and the energy eigenvalue of the bonding σ state.

energies of the atoms in jellium minus the energy of the free atom. At small densities they do, however, not in general go to zero, but approach the atomic affinity level at $-A$ if $A \gg 0$.²⁵ This is a consequence of the fact that the Fermi level of jellium goes to zero as the density goes to zero. The positive values of $\delta(R)$ in Fig. 3 correct for this wrong dissociation limit. $\delta(R)$ will go to $2A$ for R going to infinity. This is illustrated in Fig. 5.

The large R behavior of $\delta(R)$ can be understood in terms of the one-electron energy terms in Eq. (18). The two other terms go to zero as R goes to infinity. At large R (small Δn_H) the energy separation $\Delta\epsilon$ between the bound state for hydrogen in jellium and the bottom of the band increases. In the proper neutral atom dissociation limit one electron should be moved from the H^- -like state to the vacuum level (the bottom of the band). This corresponds to a one-electron energy contribution to $\delta(R)$ of $\Delta\epsilon$. Since $\Delta\epsilon$ in the local density approximation to the atomic affinity,²⁶ this gives the correct limiting behavior of $\delta(R)$.

The above arguments have mainly been meant to serve as evidence that we can understand the behavior of $\delta(R)$ and that the size of the correction terms, as calculated in the theory is of the correct order of magnitude. On this background it is not unreasonable for simplicity to directly take $\delta(R)$ from the definition Eq. (13). As mentioned above this is the approach we shall take in the following.

B. H_2 in jellium

Before considering the H_2 molecule outside a metal surface it is illustrative to first consider it embedded inside a particularly simple metal, jellium. Bulk jellium is characterized by one parameter, the electron density n_0 . When n_0 increases from zero the H_2 binding energy changes drastically. Results from a fully self-consistent calculation with $R = 1.4 a_0$ are shown in Fig. 6. Notice that the H_2 energy varies linearly with density just like for the rare gases.²⁴

In Fig. 6 the energy

$$E_B(R, n_0) = 2E_c[n_H(R) + n_0] + \delta(R) \quad (20)$$

with $\delta(R)$ taken directly from the free molecule calculation is also shown. It is seen that the E_c term describes the strong

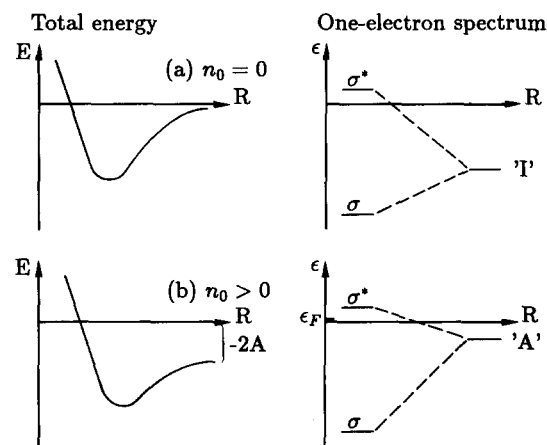


FIG. 5. Schematic illustration of the difference between the dissociation behavior of a H_2 molecule in vacuum and in jellium.

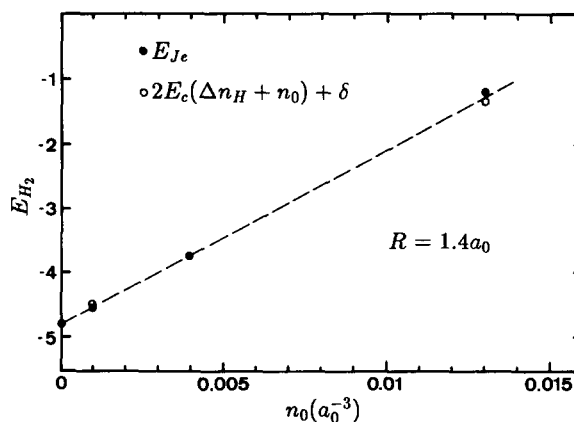


FIG. 6. The H_2 binding energy in jellium as a function of the electron gas density. Both the results of a self-consistent calculation (from Ref. 16) with the correction terms introduced in Ref. 2 and the effective medium result is shown.

effect of the electron gas on the H-H bond very accurately. It would therefore be tempting to just use this $\delta(R)$ for all situations as suggested by Daw *et al.*¹⁴ There is, however, a problem at large R . If we define a $\delta(R)$ in jellium for $n_0 = 0.0039$ like in Eq. (13) with $E_{H_2}^{\text{exact}}$ taken from the molecule-in-jellium calculation then we get the result shown dashed in Fig. 3. As evidenced by Fig. 6 the δ 's agree for small R , but for large R the dashed curve goes smoothly to zero. This is not difficult to understand given the analysis of the large R behavior of $\delta(R)$ given in the preceding subsection. When the molecule is embedded in jellium, the problem with the "wrong" dissociation limit does not exist any more and the correction term should therefore not become positive for large internuclear separations.

The key to the difference between the free molecule and the molecule in jellium lies in the fact that when the molecule is embedded in jellium of $n_0 = 0.0039$ ($r_s = 3.93$) the antibonding molecular state is filled. This is illustrated in Fig. 7. The p (or ungerade) projection of the Σ -type density of states shows a distinct resonance which follows the bottom of the band as the surrounding density increases. In vacuum ($r_s = \infty$) the resonance is empty but at higher densities it is filled. It must be emphasized that the change in the total density of states is small. Due to the Friedel sum rule it must integrate up to zero below the Fermi level. All electrons that are transferred to the molecular level are taken from metal states of approximately the same energy. The filling of the antibonding level therefore has a very small effect on the one-electron energy difference in $\delta(R)$ at small R . But the fact that it is filled means that the level should also stay filled for large R and therefore $\delta(R)$ must go smoothly to zero.

The other two terms in $\delta(R)$ cannot depend strongly on the jellium density since the surroundings do not enter explicitly. The behavior of $\delta(R)$ for a molecule with a filled antibonding level is thus also understandable.

C. H_2 outside a metal surface

For H_2 outside a metal surface a combination of Eqs. (7), (11), and (18) gives

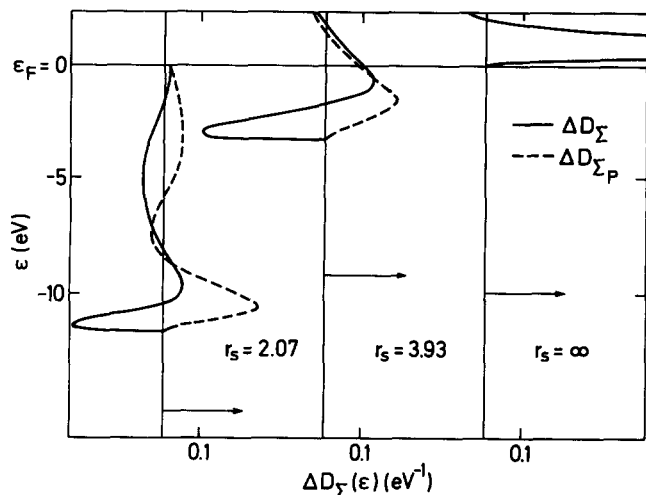


FIG. 7. The H_2 -induced density of states in jellium at various densities. Both the Σ and the $\Sigma_u = \Sigma_p$ projections are shown. From Ref. 16.

$$\Delta E_{\text{tot}} = \sum_i E_{c,i}(jn_i) + \Delta E_{\text{AS}}^{\text{MM}} + \Delta E_{\text{1el}} + \delta(\mathbf{R}, \mathbf{r}_{\text{H}_2}). \quad (21)$$

The sum runs over all atoms in the system (metal and hydrogen), $\Delta E_{\text{AS}}^{\text{MM}}$ is the total metal-metal atomic sphere correction energy, $\Delta E_{\text{AS}}^{\text{MA}}$ is the atomic sphere correction energy for the two hydrogen atoms with the metal atoms, ΔE_{1el} is the one-electron energy difference Eq. (10) due to the adsorbate-metal interaction, and $\delta(\mathbf{R}, \mathbf{r}_{\text{H}_2})$ is as usual the three last terms in Eq. (18). The last term now, in principle, depends both on the interatomic distance, the orientation of the molecule, and the position of the center of mass. The only new concept that remains to be introduced is the choice of δ function for the molecule on surface problem. We start by discussing this and then go on to discuss each of the five terms in Eq. (21) in detail.

When a molecule approaches a metal surface the antibonding molecular levels are shifted down and eventually filled. For CO, O_2 , and N_2 the $2\pi^*$ levels of the adsorbed molecules are partially filled and during dissociation they fill completely leading to adsorbed atoms with valence levels well below the Fermi level. For H_2 the filling of the antibonding σ^* level is illustrated in Fig. 8, which is taken from a self-consistent calculation for H_2 outside jellium analogous to the H_2 in jellium calculation used above. The antibonding level is seen to follow the effective one-electron potential closely, something which can also be observed in Fig. 7. Based on the discussion in the preceding subsection it must be expected that the δ function shifts from the free molecule (empty antibonding level) to the molecule-in-jellium (filled antibonding level) form as the antibonding level is filled. We therefore choose to simply interpolate linearly between the two forms:

$$\delta(R) = n_{\text{ab}} \delta_{\text{filled}}(R) + (1 - n_{\text{ab}}) \delta_{\text{empty}}(R). \quad (22)$$

The degree of filling of the antibonding level n_{ab} is calculated assuming a Lorentzian resonance with a full width of 1 eV. In principle, we would need a calculation of the one-electron spectrum of the molecule outside the surface to know the position of the antibonding resonance. Again we lean on the experience gained from self-consistent calcula-

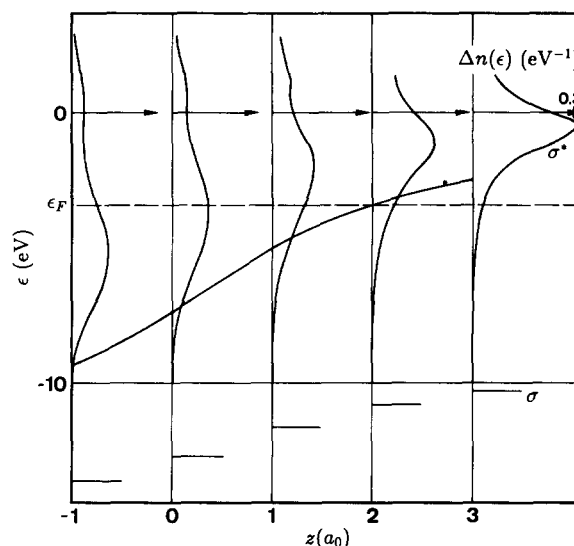


FIG. 8. The development of the H_2 density of states as the molecule approaches a jellium ($r_s = 2.65$) surface. From Ref. 2.

tions for the molecule inside and outside a jellium surface. They have shown that the antibonding resonance follows the local value of the effective one-electron potential of the undisturbed surface approximately according to

$$\epsilon_{\sigma^*}(R) = v_{\text{eff}} + Be^{-\gamma(R-R_0)} - C \quad (23)$$

with $B = 3.5 \text{ eV}$, $\gamma = 0.56 a_0^{-1}$, $R_0 = 1.4 a_0$, and $C = 1.0 \text{ eV}$.

The one-electron potential of the undisturbed surface is approximated by

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{xc}} \left[\sum_i n_i(|\mathbf{r} - \mathbf{R}_i|) \right] + \sum_i \phi(|\mathbf{r} - \mathbf{R}_i|), \quad (24)$$

where n_i and ϕ_i are the free atom density and electrostatic potentials, respectively. This is known to give a reasonable approximation to a fully self-consistent calculation for Ni(110),²⁷ but this is clearly one of the places where the approximations can easily be improved. The crossing of ϵ_{σ^*} with the Fermi level is then determined by the work function. We have taken experimental values listed in Table III.

TABLE III. Listing of the materials parameters entering the calculation. All parameters are from the atom in jellium calculation except C_d (see the text) and the experimental work functions from Refs. [29, 34, and 35].

	H	Cu	Ni
$E_0(\text{eV})$	-2.14	-3.56	-5.12
$E_2(\text{eV})$	0.28	1.33	2.14
$E_3(\text{eV})$	-0.11	-0.24	-1.00
$\alpha(\text{eV } a_0^{-3})$	84	1490	1440
$\eta(a_0^{-1})$	4.10	2.50	2.49
$\eta_1(a_0^{-1})$		0.25	0.29
$n_0(a_0^{-3})$	0.007 76	0.0115	0.0150
$s_0(a_0)$	1.71	2.58	2.46
$M(\sqrt{\text{eV} a_0^2})$	2.45	4.00	4.50
$C_{d-\sigma_f}(\text{eV})$		-3.0	-1.1
$\phi(111)(\text{eV})$		5.0	5.3
$\phi(100)(\text{eV})$		4.8	5.1
$\phi(110)(\text{eV})$		4.5	4.7

In reality we should of course have one electrostatic potential for each face studied and keep the Fermi level constant. In lack of detailed electrostatic potentials the present approach will include the main effect of changing the dipole layer outside the surface, but a more detailed description of this would be desirable.

The $\delta_{\text{empty}}(R)$ function for the free molecule is simply calculated from expression (13) using a Morse fit to the exact H_2 energy.²³ The corresponding function for a molecule with a filled antibonding state is written for $R > 1.4 a_0$ as

$$\delta_{\text{filled}}(R) = \delta_0 R \exp(-\xi R), \quad (25)$$

where $\delta_0 = -183.0 \text{ eV}$ and $\xi = 3.668 a_0^{-1}$.

The one-electron energy difference ΔE_{1el} [Eq. (10)] measures the difference in the one-electron spectrum when going from the atom in jellium to the atom outside the surface. As discussed in more detail elsewhere²² the main difference is due to the presence of the d electrons in the real solid, and the main contribution to ΔE_{1el} is due to the extra hybridization between the hydrogen states and the metal d states. We include this in a tight binding-like (resonant level) description. The model Hamiltonian is

$$H = \sum_{sp} \epsilon_{sp} + \sum_d \epsilon_d + \sum_i \epsilon_i + \sum_{i,sp} V_{i,sp} c_i^+ c_{sp} + \text{hc} \\ + \sum_{i,d} V_{id} c_i^+ c_d + \text{hc}, \quad (26)$$

where the sums are over the states of the sp bands, the d bands and the adsorbate states i .

The one electron energy difference we are after is the difference in the sum of one-electron energies with and without V_{id} included. It can be written^{22,28}

$$\Delta E_{\text{1el}} = 2 \sum_i \frac{1}{\pi} \int_{-\infty}^{\epsilon_F} [\eta_i(\epsilon) - n_i^0(\epsilon)] d\epsilon. \quad (27)$$

The phase shifts η_i are given by

$$\eta_i = A \tan \left[\frac{\Delta_i(\epsilon)}{\epsilon - \epsilon_i - \Lambda_i(\epsilon)} \right] \quad (28)$$

and

$$\eta_i^0 = A \tan \left[\frac{\Delta_{i0}(\epsilon)}{\epsilon - \epsilon_i - \Lambda_{i0}(\epsilon)} \right], \quad (29)$$

where

$$\Delta_i(\epsilon) = \sum_{sp} |V_{isp}|^2 \delta(\epsilon - \epsilon_{sp}) + \sum_d |V_{id}|^2 \delta(\epsilon - \epsilon_d) \quad (30)$$

$$= \Delta_{i0} + \Delta_{id}, \quad (31)$$

and

$$\Lambda_i(\epsilon) = P \int_{-\infty}^{\infty} \frac{\Delta_i(\epsilon')}{\epsilon - \epsilon'} d\epsilon'. \quad (32)$$

To a good approximation the contribution Δ_{i0} to Δ_i from the sp bands can be considered energy independent. Only Δ_{id} then contributes to Λ_i . In this approximation, Δ_i and Λ_i can be found analytically for a semielliptical d band²⁸ in terms of the average coupling matrix element V_i between level i and the metal d states

$$|V_i|^2 = \sum_d |V_{id}|^2. \quad (33)$$

In the simple tight binding approach taken here to estimate the one-electron energy difference, the two hydrogen states we consider are the bonding state $|a_+\rangle = 1/\sqrt{2}(|a_1\rangle + |a_2\rangle)$ and the antibonding state $|a_-\rangle = 1/\sqrt{2}(|a_1\rangle - |a_2\rangle)$. The corresponding matrix elements V_+ and V_- are related to the hydrogen $1s$ metal d matrix element Eq. (27) by $V_+^2 = V_-^2 = 1/2 V_H^2$. Following Anderson *et al.*²⁹ we write the hopping integrals V_{Hd} in the form

$$V_{Hd} = \eta(\hat{r}_{Hd}) \frac{M_H M_d}{r_{Hd}^3}, \quad (34)$$

where the M 's are potential parameters that only depend on the atom in question (the hydrogen and the metal), and the η 's are the Slater-Koster-type structure factors which depend only upon the bond angles.²⁹ In principle, the M 's can be obtained from the atom in jellium calculation.⁸ The calculated values are included in Table III. The values for Cu and Ni give good results for the d -band width, which is simply⁸ $W = 25 M_d^2 / s^5$ where s is the Wigner-Seitz radius (see Table I or III). The band widths for the surfaces are smaller than that of the bulk by the ratio of the coordination numbers for the surface and the bulk atoms. Using the value of M_H directly is more questionable because M 's for s states are known to have a substantial energy dependence.²⁹ We will therefore keep the functional form (28) including the separability into metal and adsorbate dependent parameters, keep the M_d 's and let M_H be a parameter which cannot be varied from one metal to another. In the next section, we start by looking at the M_H dependence of the results. Reasonable variations do not change the results significantly.

The simple resonant level approach taken here may seem oversimplified, and that would certainly also be the case if that was used to calculate the whole binding energy. The point is, however, that the simple (but physically transparent) model is only used to estimate a rather small (but important) correction of the order a few tenths of an eV.

Apart from the hopping parameters and the band width we also need the band centers C_d and the adsorbate level parameter ϵ_a to evaluate Eq. (26). The position of the band centers relative to the Fermi levels are based upon the self-consistent calculations of Andersen *et al.*²⁹ They are also shown in Table III. For Ni we have to shift these levels in accordance with the changes in the band width from one surface to another in order to keep the number of d electrons constant. The Cu d levels are shifted comparably.

The antibonding level $\epsilon_- = \epsilon_{a^*}$ varies as shown in Eq. (23). The bonding level, on the other hand

$$\epsilon_+ = v^0 - e \quad (35)$$

follows a small energy $e \approx 1 \text{ eV}$ under the effective potential v_0 (cf. Fig. 4) due to the metal and the other hydrogen atom as in Eq. (19), where the electrostatic potential and the density argument on the right-hand side must include the contributions from the metal. It is seen that Eqs. (23) and (35) approach the same value as the H-H separation goes to infinity.

The E_c functions are written

$$E_c(n) = E_0 + E_2 \left(\frac{n}{n_0} - 1 \right)^2 + E_3 \left(\frac{n}{n_0} - 1 \right)^3. \quad (36)$$

The parameters E_0 , E_2 , E_3 , and n_0 deduced from the results of Fig. 1 are included in Table III.

The density argument in the E_c function is parameterized in the following way. The contribution of an atom j to the average density in a sphere of radius s_i a distance r_{ij} away is written

$$\Delta \bar{n}_j(r_{ij}, s_i) = n_0/12 \exp[-\eta_2(r_{ij} - \beta s_0) + \eta_1(s_i - s_0)]. \quad (37)$$

The materials parameters $\eta = \beta\eta_2 - \eta_1$, n_0 and s_0 are calculated from the atom in jellium densities. η_1 is so small that it cannot be determined with sufficient accuracy in this way and is determined directly from the experimental shear modulus. The values calculated for H, Cu, and Ni are shown in Table III. $\beta = 1.81$ is a constant (the ratio of the nearest neighbor distance to the Wigner-Seitz radius in a fcc lattice). The radii are determined from the requirement that the spheres are neutral:

$$\sum_{j \neq i} \Delta \bar{n}_j(r_{ij}, s_i) = - \int_{s_i} \Delta \rho_i(\mathbf{r}) d\mathbf{r}. \quad (38)$$

Here $\Delta \rho_i$ is meant to include both the electron and nucleus charge from atom i . In a close-packed (fcc) structure the neutral (Wigner-Seitz) spheres are almost space filling. If we assume they are, and only include density contributions from nearest neighbors then from the overall charge conservation the right-hand side of Eq. (32) must be $12\Delta n_i(\beta s_i, s_i)$ (βs_i is defined above as the interatomic distance in a fcc lattice with Wigner-Seitz radius s_i). This gives an implicit equation for s_i which can be solved explicitly if there is only one kind of atoms⁸ and must be solved iteratively otherwise.

The density contribution of one hydrogen atom at the position of the other is written

$$\Delta n_H(R) = A \exp(-\nu R) \quad (39)$$

with $A = 0.596 a_0^{-3}$ and $\nu = 2.32 a_0^{-1}$ determined from the atom in jellium calculation.

The atomic sphere correction between metal atoms can be written⁸

$$\Delta E_{AS}^{MM} = \sum_i \alpha_i \left[\bar{n}_i - \sum_{j \neq i} \Delta \bar{n}_i(r_{ij}, s = r_{ij}/\beta) \right], \quad (40)$$

where α_i [Eq. (9)] is again a materials constant that can be determined from the atom in jellium calculation. It is included in Table III.

Finally, the contribution to ΔE_{AS}^{MA} from a metal-hydrogen pair is parameterized in the form

$$\Delta E_{AS}^{MA} = \Omega_{MA} V \exp(-\phi_M s_M - \phi_A s_A - \phi_r r_{MA}). \quad (41)$$

Ω_{MA} is the volume of overlap between the spheres of radius s_M and s_A a distance r_{MA} apart. For both H-Cu and H-Ni we get to a good approximation $V = 1860 \text{ eV } a_0^{-3}$, $\phi_M = 0.74 a_0^{-1}$, $\phi_A = 1.54 a_0^{-1}$, and $\phi_r = 1.83 a_0^{-1}$.

IV. RESULTS

In the following we shall illustrate the applicability of the approach by a couple of examples of H_2 adsorption on Cu and Ni surfaces. A detailed study of the adsorption process

TABLE IV. Atomic chemisorption energies and activation energies for H_2 dissociating over the bridge site into the center sites on the (100) surfaces of Cu and Ni as a function of the hopping matrix element parameter for H.

M/ M_H	E_a (eV)		E_{chem} (eV)	
	Cu(100)	Ni(100)	Cu(100)	Ni(100)
0	0.25	0.23	-2.40	-2.49
0.50	0.22	0.12	-2.42	-2.54
0.75	0.19	0.05	-2.43	-2.66
1.00	0.14	0.00	-2.44	-3.15

and comparison to experiment will be published separately.²¹ Here we concentrate on some trends: why is Ni much more active than Cu in dissociating hydrogen,¹⁷⁻¹⁹ how does the barrier for dissociation depend on the position of the molecule in the surface unit cell, and why are open surfaces more active than close packed ones?¹⁷⁻¹⁹

The dependence of the results on the adsorbate-metal d coupling matrix element M_H is illustrated in Table IV. Both the chemisorption energy and the activation energy depend on the value of M_H , but none of the trends that we concentrate on here do (excepting the pathological choice of $M_H = 0$, which would wash out the differences between Cu and Ni). We therefore choose one value for the rest of the presentation. The value chosen is 0.75 times the value calculated directly from the atom in jellium solution and shown in Table III. This is chosen since it gives the closest agreement with the experimental value for the difference between the atomic chemisorption energies on Cu and Ni (cf. Table II).

The difference between Cu and Ni is illustrated in Figs. 9 and 10, where the potential energy surface for H_2 dissociat-

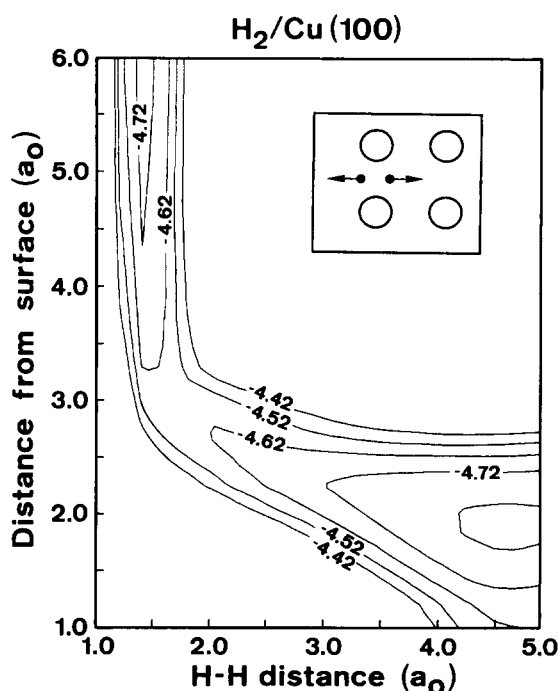


FIG. 9. Potential energy contours for a H_2 molecule approaching a bridge site on a Cu(100) surface. The molecular axis is kept parallel to the surface and the molecule dissociates into the adjacent center sites. The calculation is done for a 4×4 surface unit cell.

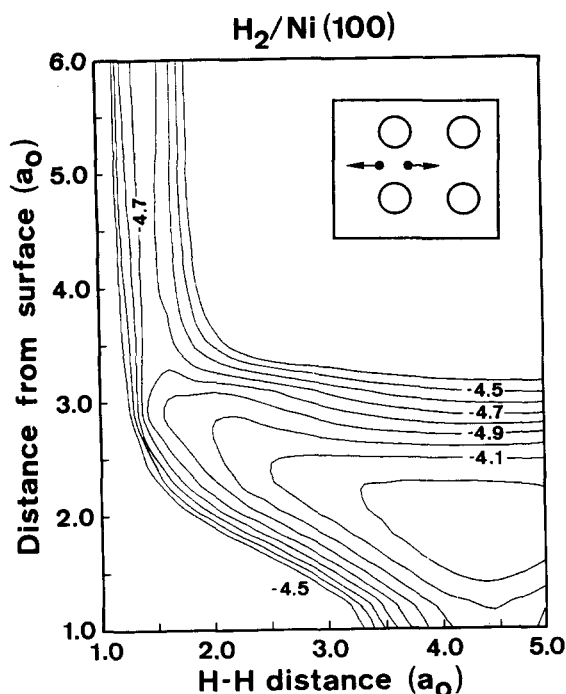


FIG. 10. Potential energy contours for a H_2 molecule approaching a bridge site on a Ni(100) surface. The molecular axis is kept parallel to the surface and the molecule dissociates into the adjacent center sites. The calculation is done for a 4×4 surface unit cell.

ing over the bridge site on the (100) surfaces of Cu and Ni are shown. The two potentials are seen to be very different. On Cu(100) the adsorption is activated whereas on Ni(100) the barrier is very low. This is in good qualitative agreement with experiment.^{17-20,30}

The results in Figs. 9 and 10 are qualitatively similar to those found in a local density calculation by Harris and Andersson⁵ for H_2 outside Cu_2 and Ni_2 clusters. They differ at the quantitative level, though. The main difference is that Harris and Andersson find a higher barrier for dissociation on Cu_2 than found in the present work. This may be due to the approximate nature of the present approach, but may also be related to the difference in the systems studied. The dimers can only be regarded as crude models of a semiinfinite surface. The results found here for H_2 on Ni(111) are very analogous to the results of Muller⁶ for H_2 on a nine-atom Pt cluster.

The difference between Cu and Ni arise in the present description almost exclusively from the one-electron energy difference. The E_c term gives rise to a repulsive interaction between the molecule and the surface. The hydrogen atoms already provide more than enough electron density to each other at the gas phase equilibrium separation that the contribution from the surface only moves the energy further up the repulsive high density part of the E_c function of Fig. 1. This tendency is also seen in Fig. 6 and is completely analogous to the picture found for rare gases approaching a metal surface.²⁴ The repulsion is dominated by the kinetic energy cost of orthogonalizing the hydrogen states to the metal states. This term is basically the same for the two metals. The inter-

action between the antibonding H_2 level and the metal d bands is very different, though. The d bands are higher in energy in Ni than in Cu and consequently the interaction is stronger. This is clearly seen in Table IV. When the coupling to the d bands is switched off, the two metals give rise to almost the same activation energy towards dissociation.

This picture of the difference between Cu and Ni is essentially identical to the one first suggested by Lundqvist *et al.*³¹ and later used to explain the trends in the catalytic activities of the transition metals by Holloway *et al.* and Nørskov and Stoltze.^{32,33} Based on their cluster calculations Harris and Andersson⁵ have proposed an alternative picture. They also focus on the kinetic energy as the origin of the repulsion H_2 meets outside Cu, but suggest that the main difference between Cu and Ni is that in Ni, s states can be promoted into the d shell. This is more localized than the s states and consequently the repulsion due to the overlap between molecule and metal states decreases. They substantiate this by showing that if they keep the number of d holes fixed in the calculation for Ni_2 , an unfilled state exists well below the Fermi level and the interaction is at least as repulsive as for Cu. Formulated in this way it appears as if the picture is not very different from that of Lundqvist *et al.* and the present approach. If in our calculation we keep the d -occupancy fixed for Ni when the d states have been allowed to interact with the H_2 antibonding state this corresponds to not filling the resulting bonding state and ΔE_{le} would be zero.

If the potential like in Figs. 9 and 10 is calculated for each point in the surface unit cell the position dependent activation energy $E_a(x,y)$ can be calculated. From this one can construct graphs like in Fig. 11 showing the functions.

$$s(E) = \frac{1}{\Omega} \int_{\Omega} \Theta[E - E_a(x,y)] dx dy. \quad (42)$$

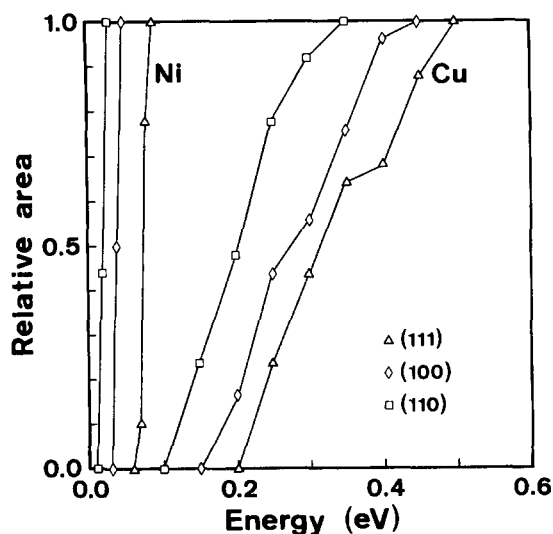


FIG. 11. The area of the surface unit cell where the activation energy is lower than a given value E shown as a function of E . The areas are normalized to the unit cell area. All three low index surfaces are shown for Cu and Ni. The activation energy over a particular site is determined as the maximum energy over a particular site along contours like in Fig. 9 or 10. The molecular axis is kept parallel to the (10) direction.

Ω is the area of the surface unit cell and $\Theta(x)$ is zero for x negative and one for x positive. $s(E)$ includes the contribution to the dependence of the sticking coefficient on the normal energy of the incoming molecule from the variation of the activation energy over the unit cell. Other effects such as the efficiency of energy transfer between the various adsorbate degrees of freedom and to the substrate and tunneling will contribute to this.²¹ The $s(E)$ functions of Fig. 11 are very similar to those deduced from beam experiments.¹⁷⁻¹⁹ One sees that the Cu surfaces have much larger variations in the activation energy than the Ni surfaces. The reason is that for Ni the very small barriers lie exclusively in the entrance channel rather far from the surface where the variations along the surface are small. On the Cu surfaces on the other hand the stability of the final (atomic chemisorption) states become important, and they vary considerably over the unit cell.

For Cu the trend in the variation of the barrier heights with crystal face is the one observed in the beam studies of Balooch *et al.*¹⁷ They find a large increase in the sticking coefficient around an energy of 0.15 and 0.20 eV for the (110) and (100) surface, respectively.

For Ni the trend in Table V is also in agreement with the observed one.^{18,19} On Ni (110) the observed barrier is zero or less. On Ni(100) and (111) the barrier in the entrance channel is slightly larger (0.05–0.1 eV).

The variation in E_a with crystal face is determined mainly by the work function. The electrostatic potential outside the surface determines when the antibonding level crosses the Fermi level. Because the barriers for all the surfaces are mainly in the entrance channel, the differences between the various crystal faces are due to this effect. If one changes the work function for, e.g., Ni(111) to be that of the (110) surface, the activation energy also changes to that of the (110) surface. On Cu the availability of suitable final states also plays a role. In particular the close packed (111) surface has a difficult geometry as seen by a dissociating H_2 molecule. For the Ni surfaces this is less of a problem because the atomically adsorbed state is more stable than the molecule everywhere in the unit cell.

V. CONCLUSIONS

In the present paper the effective medium theory has been extended to treat H_2 and in principle other molecules outside metal surfaces. The theory for molecules is less satisfactory than the one previously used to describe bulk metals, surfaces, and simple atomic adsorption on metal surfaces. For such systems it is possible to calculate most of the quantities entering from the solutions of the atom in jellium problem. To treat a molecule the theory is stretched further and we have used independent calculations for the free molecule and the molecule in jellium to determine one of the correction terms. The behavior of this term can, however, still be understood at the semiquantitative level within the theory.

The approach has two strong points. First, it is computationally simple. It is far more involved than pair potentials, but still not more demanding than it can be used dynamics simulations. The calculation of the total energy of a molecule outside a 4×4 unit cell takes about 1 s on a personal comput-

er. Second, the individual terms in the total energy expression Eq. (21) have a clear physical interpretation. This makes it simple to develop a conceptual understanding of the process studied. This has been illustrated in two cases: in the explanation of the cause for the very different behavior of H_2 outside Cu and Ni surfaces, and of the difference between various crystal faces.

The approach leaves ample room for improvements. The most pertinent ones are the inclusion of a more detailed description of the electrostatic potential outside the surfaces and a better treatment of the H_2 -metal d contribution to the one-electron energy difference.

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