## A SIMPLE QUANTUM CHEMICAL THEORY OF DISSOCIATIVE ADSORPTION

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Potential energy curves for the adsorption of a hydrogen atom on the (100), (110), (111) and the stepped (311) crystal faces of copper have been calculated in the pairwise additive model for gas atom-solid interactions. A Morse function is used to represent the lowest singlet pairwise H-Cu interaction potential and its parameters are adjusted so that the calculated maximum bond energies conform with the available experimental data. Bond strength on the low index faces is found to increase with the adatom's local coordination number. Except for the edge sites, the steps on the (311) surface strengthen the bonds to sites on the component low index facets. A systematic study of the convergence of the bond energy as a function of the number of solid atoms is reported. The H-Cu(s) potential is shown to be relatively insensitive to changes in the first layer separation distance of the size inferred from experiment. A new model for diatom-solid potentials is proposed in which the diatom-solid potential is expressed as a sum of the differences between diatom-solid atom London-Eyring-Polanyi-Sato threebody potentials and the diatom singlet potential. This model is used to calculate potential curves for various approaches of a hydrogen molecule towards the same copper faces.  $H_2$  is predicted to be physisorbed on each face. The atom-solid and diatom-solid potentials are used in conjunction with a model formulated by Lennard-Jones to estimate activation energies for dissociative adsorption. The correct order is obtained for the activation energies on the low index faces. Substantially lower activation energies are obtained for approaches toward many of the sites on the two low index facets of the (311) surface as compared to the same approaches towards the individual component faces. Dissociative adsorption is predicted to proceed without activation near the steps on this surface. In general, higher activation energies are obtained when the admolecule is perpendicular to the surface or facet in question. The simple idea that the activation energies are determined by small shifts of the atomic potential relative to the less structure-sensitive molecular potential works well for the low index faces, but is not wholly satisfactory for the stepped (311) surface. All results reported in this paper are negligibly different from those that are fully converged with respect to cluster size in the present model.

## 1. Introduction

Although the relative importance of bulk, surface and local properties in heterogeneous catalysis has yet to be resolved, it has become increasingly clear in recent

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years that local chemical bonding effects contribute significantly to this process. The most natural way to describe local bonding structure (or a surface complex) is to treat it as a molecule and to use the standard concepts and procedures of quantum chemistry. Accordingly, semiempirical [1,2] and "ab initio" [3] molecular orbital (MO) methods and the SCF-X $\alpha$  [4] method have been used in addition to model Hamiltonians [5] and perturbation methods [6] to study chemisorption. These methods are of two types: either they are computationally fast and qualitative at best or computationally slow, quantitative, and limited to a few solid atoms. The best compromise seems to be the SCF-X $\alpha$  method [4], but even that method, irrespective of whether or not it can be developed to the point where it can be used to compute reliable potential surface, is too slow to perform electronic structure calculations at *many* geometries in an economical manner. On the other hand the qualitative methods allow geometry searches to be made, but are generally too inaccurate to give results that are completely trustworthy.

Encouraged by the results of recent work on metal aggregates [7] and chemisorption [8], we have elected to investigate the dissociative adsorption of hydrogen on copper by adapting the simple approach that London, Eyring, Polanyi and Sato (LEPS) [9] used to construct a potential surface for the simplest bimolecular exchange reaction,  $H + H_2$ . The LEPS approach is a valence bond (rather than a MO) procedure and enjoys a number of attractive features [8], not least of which is the fact that the correct asymptotic behavior is obtained.

In our calculations we first assume that the solid surface can be adequately represented by a slab of the bulk crystal and later show that this assumption is well-justified. We proceed in three steps. In the first step, we express the effective interaction,  $\mathcal{U}_A$ , between an adatom, A, and the surface as the sum of pairwise interactions between the adatom and each solid atom. The two-body interaction is taken to be the lowest singlet interaction and is represented by an empirical potential function. Interaction potentials are calculated for the perpendicular approach of an adatom towards selected bonding sites. The parameters of the empirical potential function and the dimensions of the slab are adjusted in a self-consistent way so that the known bond energy data for specific crystal faces are reproduced and the total contribution of the neglected solid atoms in the semi-infinite solid is negligible.

These results, which are needed in the second step of the calculation, can also be used to calculate bond energies for other faces. In the second step, we express the interaction,  $\mathcal{U}_{AB}$ , of a diatom, AB, with a surface as the sum of interactions of the the diatom with the individual solid atoms, i.e., as the sum of three-body potential terms. The three-body potential for the diatom and a solid atom is taken to be the difference between their lowest LEPS potential and the lowest diatom potential. The three-body LEPS potentials are computed from the lowest singlet and triplet adatom—solid atom pairwise potentials and the potentials for the lowest singlet and triplet states of the diatom. We assume that the latter three two-body potentials can also be represented adequately by empirical potential functions. Since functions of this type are usually available for the diatom and the same parameter values can often be used in the two adatom—solid atom potentials, the diatom—solid interaction can be calculated immediately.

Finally, we adopt a simple model for dissociative adsorption that was introduced by Lennard-Jones [10] (LJ) and evaluate the activation energy,  $E_a$ , for this process by equating it to the energy above the asymptotic diatom energy where the diatom—solid and atom—solid interaction curves cross less the zero-point energy of the diatom.

A preliminary account of our results has been given elsewhere [11].

# 2. The adatom solid singlet interaction potential

#### 2.1. The experimental situation

Measurements of changes in surface potential which accompany the adsorption gas molecules on metals at low temperatures have done much to advance our knowledge of the chemisorption process.

A surface potential study [12] of the adsorption of hydrogen on an evaporated copper film led in the late fifties to estimates of 4-5 and 56 kcal/mole for the activation energy for dissociative adsorption and for the H-Cu(s) bond energy, respectively. At that time, it was generally assumed, in the absence of any evidence to the contrary, that such films present equal amounts of the low index faces (100), (110) and (111) to the gas phase species. However, subsequent surface potential measurements [13,14] established that copper films prepared under different conditions may exhibit quite different behavior. They also led to the conclusions that more than three faces contribute significantly to annealed copper surfaces and that one of these faces gives an almost entirely positive surface potential with hydrogen and another only negative values [14]. The positive species are less strongly adsorbed and it is likely that they can only be produced by the adsorption of atomic hydrogen [14]. The activation energy for dissociative adsorption on films representative of one extreme, viz., a negative surface potential increasing smoothly in magnitude up to the maximum coverage, was estimated to be 7-10 kcal/mole [14].

A case was made for assigning a mainly positive surface potential to the closepacked (111) face [14]. Several important conclusions appear to follow from this assignment. Taken together with the surface potential results reported for sintered films [15], it implies that the (100) face has a mainly negative surface potential. It also means that the H-Cu(s) bond is not as strong on the (111) face as on the (100) and other faces. And finally, since the original estimates of 4-5 and 56 kcal/mole for the activation energy for dissociative adsorption and for the H-Cu(s) bond energy, respectively, were made for a film with a negative surface potential, these thermochemical quantities cannot be assigned to the (111) face.

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It appears to be a general rule that the binding of adatoms is weaker on closepacked faces than on rougher ones [16]. Surface potential experiments with single crystal faces [17] suggest that the heats of adsorption and hence that bond energies for carbon monoxide on the low index faces of copper are in the sequence (110) >(100) > (111). Given these observations and the previous remarks, it seems reasonable to assume that the same order prevails for H-Cu(s) bond energies. As we shall see below (section 3.2), the proposed order is consistent with the results of molecular beam and permeation studies of the H<sub>2</sub>-Cu(s) system and therefore draws further support from them.

Both infrared spectroscopy of carbon monoxide chemisorbed on various copper surfaces and surface potential measurements for carbon monoxide chemisorbed on single crystals indicate that high index faces predominate on polycrystalline copper surfaces [18]. Surface potential experiments with atomic hydrogen on single crystal faces confirm that the (111) face gives a mainly positive surface potential and that the (100) face gives a negative surface potential [18]. The (110) face gives a mainly positive surface potential, but the (211) face gives a negative potential [18].

The isosteric heat of adsorption, 9-10 kcal/mole, reported [18] for hydrogen on Cu(311) implies an approximate value of 56-57 kcal/mole for the H-Cu(s) bond energy on the (311) face. To the best of our knowledge, the heat of adsorption of hydrogen has not yet been reported for any other single crystal face of copper. It is hoped that the present theoretical work will stimulate experiments that will provide such data.

#### 2.2. Calculations and results

We assume that the lowest singlet pairwise H-Cu potential is adequately described by a Morse potential function:

$${}^{1}u(r) = {}^{1}u_{0} \left\{ \exp\left[-2{}^{1}\beta(r-r_{0})\right] - 2\exp\left[-{}^{1}\beta(r-r_{0})\right] \right\},$$
(1)

where r is the internuclear separation.  ${}^{1}u$  has the minimum value of  $-{}^{1}u_{0}$  at  $r = r_{0}$ ;  ${}^{1}\beta$  determines the shape of the curve.  ${}^{1}u_{0}$ ,  $r_{0}$  and  ${}^{1}\beta$  can be adjusted so that the adatom—solid potential conforms with the experimental data. We proceeded to do this in the following way. First, we inspected each of the (100), (110), (111) and (311) faces and located the bonding sites which enable one to map out the general form of the interaction potentials with a minimum amount of effort. These sites are readily identifiable and are shown in fig. 1 along with the interplanar distances, d, in the bulk solid. It should be noted that sites 3 and 5 on the (111) face are not equivalent because atoms are located directly below site 3 but not site 5 in the second layer and directly below site 5, but not site 3 in the third layer [19]. Also, the (311) surface is a stepped surface and is therefore more complicated than the three low-index surfaces. In the more descriptive notation of Somorjai and his coworkers [20], it is denoted by Cu(S)-[2(100) × (111)] which indicates that it con-



Fig. 1. The faces and sites that were studied. The full dots denote metal atoms. Fig. (ivb) shows the (100) (111) facets of the (311) face. *a* and *d* are the lattice parameter and the bulk interlayer spacing, respectively. The coordinates of the sites are as follows: (100): 1(0,0);  $2(a/(2\sqrt{2}), 0)$ ;  $3(a/(2\sqrt{2}), a/(2\sqrt{2}))$ .

(110) : 1(0,0); 2(a/(2 $\sqrt{2}$ ), 0); 3(0, a/2); 4(a/(2 $\sqrt{2}$ ), a/2) (111) : 1(0,0); 2(a/(2 $\sqrt{2}$ ), 0); 3(a/(2 $\sqrt{2}$ ), a/(2 $\sqrt{6}$ )); 4(3a/(4 $\sqrt{2}$ ), 3a/(4 $\sqrt{6}$ ); 5(a/ $\sqrt{2}$ , a/ $\sqrt{6}$ ). (311) : 1(0,0); 2(a/(2 $\sqrt{2}$ ), 0); 3(a/(2 $\sqrt{2}$ ),  $\sqrt{11a}/(4\sqrt{2})$ ); 4(3a/(4 $\sqrt{2}$ ),  $\sqrt{11a}/(4\sqrt{2})$ ). In the present work, a = 3.61 Å.

sists of (100) terraces, two atomic rows wide, separated by (111) steps, one atomic layer high. The bonding sites enumerated for the (311) surface thus consist of those enumerated for the (100) and (111) surfaces plus others peculiar to the (311) surface.

Next we adopted a simply truncated solid model for the surfaces. If such a surface is penetrated at right angles to the surface, a plane parallel to the top one will be found such that the atoms of the top plane can be superposed on the atoms of the lower plane by a simple displacement in the direction of penetration. The same will hold for the atoms of the next lower plane and the first plane below the top plane, and so on. The surface is thus composed of a group of parallel planes which repeats itself over hand over again. The repeating units of the (100), (110), (111) and (311) surfaces consist of 2, 2, 3 and 11 planes, respectively. In order to determine how many atomic planes should be included explicitly in the calculation, one

should ideally consider an integral number of these repeating units. However, since the object of our work is to produce good interaction potentials as efficiently as possible, only three planes were considered in the preliminary calculations [21a]. It was felt that this number of planes should be enough to enable one to distinguish adequately between the sites on the low index surfaces and to develop a satisfactory feeling for the general form of the interaction potentials.

Each plane was constructed by adding atoms in a spiral fashion to two-dimensional lattice cells like those shown in fig. 1. In the preliminary calculations [21a], this process was terminated following the construction of three finite two-dimensional lattices of  $7 \times 7$  atoms. Interaction potentials were then calculated for the perpendicular approach of a hydrogen atom towards each of the selected bonding sites on the three low-index surfaces. We varied the distance, R, between the adatom and the site in increments of 0.1 Å. The three parameters of the Morse potential were varied until (1) the maximum bond energy on the (111) surface was 56-57 kcal/mole and (2) the order of (maximum) bond energies on the low-index surfaces was (110) > (100) > (111). The parameters were sensitive enough to these two constraints for them to be determined with some precision. The maximum bond energies on the (100) and (110) surfaces were always found to exceed that for the (111) surface, but the order of the former two depended on the parameter values. The final parameters are given in the first row of table 1.

These parameters have been used to perform a systematic investigation of bond energy for the three low-index surfaces as a function of site, the number of planes, and the number of atoms per plane and for the (311) surface as a function of site and the number of planes. Approaches to bonding sites on the (100) and (111) facets of the (311) plane were made normal both to the facet in question and to the (311) plane. Adopting the criterion that the bond energies for all sites and approaches that we studied should not change by more than 0.01 eV when another plane is added to the surface and when another row and another column of atoms are added to each plane, we found that 5, 6, 4 and 7 planes must be included explicitly in calculations for the (100), (110), (111) and (311) surfaces, respectively, and that 49 atoms per plane must be included explicitly. This means in effect that in the present model one should include all planes to a depth of ca. 7.5 Å explicitly in the calculations. Recently, the convergence properties of several other chemisorption models have been examined systematically as a function of cluster size [3a,b,22].

Table 1

Parameters for	the lowest	singlet	pairwise	H-Cu	Morse	potential
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	$^{1}u_{0}$ (eV)	r <sub>0</sub> (Å)	<sup>1</sup> β (Å <sup>-1</sup> )	
Preliminary work [21a]	0.316	2.3	1.2	
Present work	0.316	2.34	1.43	
Olander [24]	0.061	4.60	0.60	

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In the present model, edge effects can be investigated by calculating the bond energies for sites that would have been equivalent had the semi-infinite solid been the substrate. The difference in the bond energies provides a measure of the magnitude of the edge effects and also serves as a test for convergence with respect to cluster size. Edge effects were found to be more pronounced for the clusters with an odd number of atoms in each plane. In these cases, the center of the lattice cell containing the bonding sites is not the center of symmetry of the top plane. Other, less important, edge effects arise from the relative disposition of the finite planes and could have been investigated by altering that disposition. We have carried out all subsequent calculations with 64 atoms per plane and included all planes to a depth of 7.5 Å. It should be noted, however, that, had the calculations been carried out with 36 atoms per plane, there would have been a significant saving of computer time at the expense of a relatively small loss of numerical accuracy. The inclusion of more than three planes in the calculations results in significant increases in the bond energy differences between different sites on the rougher faces.

As this investigation was completed, Pritchard et al. [18], published results which leaves little doubt that our initial assumption that the bond energy on the Cu(111) face is 56-57 kcal/mole is incorrect. Therefore, a search was undertaken for parameter values that give interaction potentials that are in better accord with the available experimental data. Keeping  ${}^{1}u_{0}$  fixed and restricting the calculations to those sites identified as the maximum bond energy sites by the previous parameters, we varied  $r_{0}$  and  ${}^{1}\beta$  until (1) the maximum bond energy on the (311) surface was ca. 56-57 kcal/mole, (2) the order of (maximum) bond energies on the low-index surfaces was (110) > (100) > (111) and (3) the order of (maximum) bond energies on the (311) and (111) surfaces was (311) > (111). As before, the parameters were found to be quite sensitive to constraints of this type. For example, when the parameters were first varied coarsely, two sets of parameter values, as shown in table 2, were found to satisfy the first two constraints almost equally well. However, only set (b) satisfies the third constraint and was considered further. The final parameters are given in the second row of table 1.

Table 2

Intermediate results obtained during search for new parameters for the lowest singlet pairwise H-Cu Morse potential in better accord with experiment; the following notation is used: plane: site [approach]: bond energy [eV] (bond distance [Å])

(a)	$r_0 = 2.7 \text{ Å}, \ ^{1}\beta = 1.2 \text{ Å}^{-1}$
	(100): 3: 2.84 (1.6); (110): 4: 3.26 (1.1); (111): 3: 2.69 (1.9);
	(311): 2" [1(111)]: 2.50 (1.75)
(b)	$r_0 = 2.3 \text{ A}, \ ^1\beta = 1.4 \text{ A}^{-1}$
	(100) : 3 : 2.25 (1.0); (110) : 4 : 2.53 (0.7); (111) : 3 : 1.96 (1.5);
	(311): 2'' [1(111)]: 2.57 (1.55).

Table	3
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H-Cu(s) bond energy [eV] (bond distance [Å]) calculated as a function of surface, site, and approach with the Morse parameters determined in the present investigation; the maximum bond energy calculated for each surface is underlined

Site	Surface										
	(100)	(110)		(111)	(311)						
1	1.2939 (2.0	)) 1.0455	(2.0)	1.4529 (2.0)	0.9936 (2.1)						
2	1.6496 (1.3	7) 1.3551	(1.7)	1.8250 (1.6)	1.2918 (1.7)						
3	2.1739 (1.2	2) 2.1965	(0.8)	1.9134 (1.6)	2.3232 (0.8)						
4		2.4919	(0.8)	1.8251 (1.6)	2.3232 (0.8)						
5				1.9130 (1.6)							
(311)			<u> </u>	·····							
(100) 1	Facet		(111)	Facet							
Site	Approach		Site	Approach							
	1(100)	⊥(311)		L(111)	L(311)						
1'	1.1552 (2.1)	0.9936 (2.1)	1"	1.0694 (3.35)	2.1967 (2.0)						
2'	1.4540 (1.7)	1.2918 (1.7)	2″	2.4423 (1.55)	2.4008 (1.7)						
3'	2.1052 (1.7)	1.3382 (2.1)	3″	2.5061 (1.6)	1.4816 (2.1)						
4'	2.5649 (1.2)	1.8649 (1.5)	4″	2.1920 (1.7)	1.3680 (2.1)						
5'	1.4879 (2.6)	2.1967 (2.0)	5"	2.0325 (1.6)	1.4277 (1.9)						
~ 1	1 0466 (2 2)	2 4000 (1 7)	C"	2 1010 (1 7)	1 2670 (2 1)						

The bond energies,  $\mathcal{U}_{A}(\infty) - \mathcal{U}_{A}(R_{\min})$ , and bond distances,  $R_{\min}$ , that were calculated with these parameters are listed in table 3. (Note that  $R_{\min}$  is generally different from the shortest distance between the adatom and a surface atom). We have compared the new results with the old ones. The same order is obtained for the bond energies calculated for the sites on the low index surfaces, but not for the sites on the (311) surface. Approaches towards two sites not far removed from the bottom of the step, along the normals to the facets in question, are calculated with the new parameters to have slightly greater bond energies than the site and approach identified by the old parameters as the one with maximum bond energy. In particular, the maximum bond energy that is calculated for the (311) surface with the new parameters is obtained when the adatom approaches site 4' along the normal to the (100) facet. This energy exceeds that calculated for the (110) surface by less than 2 kcal/mole, but exceeds those calculated for the (100) and (111) surfaces by substantial amounts. On the basis of these results and the simple thermochemistry of dissociative adsorption, we would expect the (110) surface to adsorb molecular hydrogen almost as strongly as the (311) surface, the (100) surface to adsorb molecular hydrogen but only weakly, and the (111) surface to fail to adsorb molecular hydrogen completely, at low temperatures. No contradictions arise if we identify the (111) face with the face in the surface potential experiments [14] which seemed only able to adsorb atomic hydrogen.

The order of the bond energies calculated for the sites on the low index surfaces correlates well with the number of nearest neighbours, i.e., with the adatom's local coordination number. Thus, the sites which form the strongest H-Cu(s) bonds are the sites with a maximum local coordination number of 4 on the (100) and (110)surfaces and 3 on the (111) surface. The distances between the adatom in its minimum energy configuration and the nearest surface atom on the (100), (110) and (111) faces are 2.2, 2.1, and 2.2 Å, respectively. They are considerably larger than the sum of the atomic radii. As expected, binding is more uniform on the closepacked (111) surface than on either of the rougher (100) and (110) surfaces. The bond energy calculated for site 3 on the (111) surface is slightly larger than that calculated for site 5, but the difference is negligible. Sites 2 and 4 on this surface are equivalent. Except for the "edge" sites, i.e., the sites located on the top (311) plane around the perimeter of the lattice cell under consideration, and for one or both sites at the bottom of the step, the bond energies calculated for sites on the (311) surface are greater than those calculated for the corresponding sites on the component low index faces when the approach is made perpendicular to the facet in question, and the bond energy calculated for this approach is greater than that calculated for the approach perpendicular to the (311) surface. Roughly speaking, the nearer the site to the bottom of the step, the stronger is the bond formed with the adatom.

It is reassuring that the results reported in table 3 and the old ones share many common features. However, they differ not only in how well they conform with the bond energy data available from experiment, but also in two other important aspects. Firstly, the new parameters generally lead to longer and probably more reasonable bond distances. The change in the equilibrium adsorption distance is by far the most dramatic for the maximum bond energy site on the (100) surface and the corresponding site on (100) facet of the (311) surface for an approach normal to that surface. Secondly, one infers from the new results that the order of the activation energies for surface migration on the low index surfaces is (100) > (110) > (111), but from the old results that the order is  $(100) \ge (111) > (110)$ ,  $(111) \sim (110)$ .

#### 2.3. Discussion

Several previous investigations [23] of adatom-metal interactions are similar in many to the present one. Goodman [23a] used the pairwise additive model and a LJ 6-12 interatomic potential to calculate the interaction potential between a gas atom and the (100) and (110) faces of a cubic lattice. A summary of earlier work with this model can also be found in this paper along with an assessment of the

model's validity.

Olander [23b] used the pairwise additive model to describe hydrogen-metal interactions, but whereas Goodman's study and the present work are concerned only with surface interactions, Olander examined both surface and bulk interactions between hydrogen and the metal. He included metal-metal interactions in his calculations and represented them as well as the hydrogen-metal interactions by Morse potential functions. The parameters of the hydrogen-metal potential functions were determined from the experimental values for one surface and two bulk properties of the hydrogen-metal system. He treated several metals and studied two of their crystal faces. In particular, he investigated the (110) and (111) surfaces of (fcc) copper and nickel.

The surface property used to determine the hydrogen-metal parameters was the heat of adsorption and it was assumed that it applied to the face under consideration. The parameters, however, proved to be more sensitive to the structure of the bulk crystal than to the nature of the adsorption face. The averages of the values that Olander obtained for the hydrogen-copper parameters are given in the third row of table 1. They correspond to a weaker and to a longer range potential than do ours. As a consequence, Olander's calculations predict that the difference in the bond energy between the (110) and (111) faces is only 3% of the bond energy and that the bond distances for the preferred adsorption sites are more than an angstrom longer than those calculated here. Both sets of calculations predict a small difference in the bond energies for sites 3 and 5 on the (111) surface, but Olander's predict the hydrogen adatom to be slightly more tightly bound to site 5 (no metal atom directly below the adatom in the first sublayer). One other possibly unsatisfactory aspect of Olander's calculations is that they suggest that the adsorption and migration positions on the (111) surfaces of copper and nickel are the reverse of those expected.

In a study similar to Goodman's [23a], Bacigalupi and Neustadter [23c] (BN) used the pairwise additive model and the LJ interatomic potential to investigate the adsorption of an adatom on a fcc substrate. They calculated the interaction energy at a large number of sites on each of the eight surface planes of highest atom density for specific values of  $\sigma/a$ , where  $\sigma$  is the finite value of r at which the LJ adatom—solid atom pairwise potential vanishes. The (111), (100), (110) and (311) planes are the four highest atom density planes in order of decreasing density. This order is just the reverse of that proposed here for the H—Cu(s) bond energies. Only adatom approaches normal to the face were considered. As  $\sigma/a$  increases, the maximum bond energies increase, but the spread in their values for the four specified planes narrows and some re-ordering takes place. Thus, for  $\sigma/a = 0.6$ , the normalized bond energies are (100) = 1.387, (110) = 1.657, (111) = 1.182, (311) = 1.712 and, for  $\sigma/a = 1.0$ , they are (100) = 3.08, (110) = 3.128, (111) = 3.132 and (311) = 3.256.

The present results and Olander's can be compared directly with BN's by fitting a LJ interatomic potential to the Morse interatomic potentials at the minimum  $r_0$ .

The present (Olander) Morse potential is then found to correspond to a LJ potential with  $\sigma = 2.08$  (4.10) and  $\sigma/a = 0.58$  (1.14). Both sets of results can be seen to be in essential agreement with those of BN. The present bond energies are greater than those calculated by BN because the Morse potential falls off more slowly than the LJ potential near the well minimum.

Goodman [23a] reported that the preferred adsorption sites on the (100) and (110) faces are independent of  $\sigma/a$  over a wide range, but there is evidence from Olander's results and the present ones that this does not hold for the (111) and (311) faces. The present work also shows that the shape of the interatomic potential as well as the location of its minimum can exert an important influence on the final results.

The pairwise additive model assumes a substrate composed of atoms with spherically symmetric charge distributions. Copper, which is very nearly a completely filled 3d shell and a single 4s electron, forms one such substrate. Chemisorption of atomic hydrogen on nickel, a metal with one fewer valence electron and an incomplete 3d shell, is less likely to be represented adequately by the pairwise additive model. The observed heats of adsorption of 23 kcal/mole for H<sub>2</sub> on Ni (100) [24a,b] and Ni (111) [24b,c] and of 21.5 [24c] (20.3 [24d]) kcal/mole for H<sub>2</sub> on Ni (110) seem to confirm this. An examination of table 1 in BN's article [23c] leads to the conclusion that it is impossible to account for the H-Ni (s) bond energies implied by these results in term of the pairwise additive model and a LJ interatomic potential characterized by a realistic value of  $\sigma/a$ .

Nevertheless, experimental [12,24e] and theoretical [2a-c] data exist which imply that the nickel s-orbitals are mainly responsible for the H-Ni(s) bond and that the nickel d-orbitals play a less important role. We shall therefore compare the present results for the H-Cu(s) system with results previously reported for the H-Ni(s) system. Blyholder [2a] carried out CNDO MO calculations for hydrogen atom adsorption on the low index faces of nickel clusters containing up to 10 metal atoms. He concluded (i) that the bond energies on each face increase with the local coordination number of the adatom, (ii) that the maximum bond energies decrease in the order (111) > (110) > (100), and (iii) that site 5 on the (111) surface is the preferred adsorption site. These conclusions can be criticised not only because many of the adsorption sites that were considered do not possess their correct nearest neighbor environment [2b,22a], but also because the differences between the results reported for the clusters and those for the semi-infinite substrate are unlikely to be negligible.

Fassaert and Van der Avoird [2b] (FA) reported modified extended Hückel (EH) calculations for hydrogen atom adsorption on nickel clusters containing up to 14 atoms. An extra term representing the repulsion between the adatom and the metal atom cores was included in the Hamiltonian. They concluded (i) that the bond energy on the (100) face decreases as the coordination number increases, (ii) that the bond energy for site 1 on each face decreases in the order (110) > (100) > (111), and (iii) that the hydrogen atom is more strongly bound to edge sites than to notch sites on stepped surfaces.

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The EH model is thus in disagreement with both the CNDO model and the pairwise additive model over how the bond energy on the (100) face varies with the adatom's local coordination number. The EH model is also in conflict with the pairwise model over whether the hydrogen atom forms stronger bonds with edge or notch sides. FA [2b] cite data obtained in a study [25a] of hydrogen atom chemisorption on Raney-nickel by neutron inelastic scattering (NIS) as evidence confirming the EH predictions. The NIS spectra were obtained on the energy-gain side and exhibited poor resolution in the region where the bands produced by hydrogen were detected. They were indeed interpreted in terms of a hydrogen atom bonded to only one nickel atom, but the presence of more than one chemisorbed state was not considered. It was also overlooked that the vibrational frequency assigned to the Ni-H bond is inconsistent with vibrational data for transition metal hydrides with terminal M-H bonds. Subsequently, better resolved, energy-loss, NIS spectra were reported from the same laboratories [25b], the spectra compared with vibrational spectra for the transition metal hydrides, and the conclusion drawn that most of the hydrogen chemisorbed on Raney-nickel is highly coordinated.

These questions may not be settled yet, however, because Nakata [25c] has apparently observed a fundamental infra-red absorption band for hydrogen chemisorbed on dispersed nickel near the band in the NIS spectrum that was assigned to a two quantum process [25b].

# 2.4. The adequacy of the surface model: the effect of reconstruction

As a necessary first step, the surface has been treated simply as a truncated bulk crystal. The semi-infinite lattice is a better model. Furthermore, the overall interaction between a gas atom and a semi-infinite lattice that results from the summation of pairwise gas atom—solid atom interactions over all lattice sites can be expressed in closed form [26]. The special cases of the Yukawa [26] and Morse [27] pairwise potentials have been worked out in detail. However, the present approach enjoys the advantage of greater flexibility: other effects such as distortion of the lattice due to the presence of the surface can be taken into account easily. Moreover, it can be shown that the total contribution to the gas atom—surface bond energy by the solid atoms that were not considered explicitly in the present calculations is negligibly small (see Appendix). Thus, in contrast to the quantum chemical models for chemisorption [1-4], results that are negligibly different from the fully converged ones are readily accessible in the present model.

Comparison of calculated and measured low energy electron diffraction (LEED) intensity profiles for the low index faces of (fcc) aluminum indicates that the Al (110) and possibly the Al(111) surfaces can be treated as simply truncated, but otherwise perfect bulk solids [28]. However, the spacing between the outermost two layers of the Al(100) surface is found to be contracted from the bulk interlayer spacing by 10-15%. The position of the Al(111) surface is, to within less than 5%, identical to the position it would have if the bulk of the crystal were simply ter-

minated. Model calculations based on the Hellman-Feynman theorem predict contractions of a similar magnitude, but in the order (110) > (100) > (111) [29]. The validity of these calculations has been questioned because certain crystal effects of comparable magnitude were not considered [30]. Medium energy electron diffraction intensity calculations that were reported very recently favor a smaller contraction of 5% for the Al(110) surfaces [31]. The validity of the interpretation of the LEED data in terms of a surface contraction is itself uncertain. Laramore et al. [32] were able to account qualitatively for the Al(110) LEED data by proposing that stepped regions exist on the surface.

In an earlier theoretical study [33], surface distortions were calculated for the low index faces of a series of fcc metals including Al, Cu and Ni by minimizing the surface energy in a pairwise additive model. These calculations predict that the top two layers do not contract towards the bulk, but dilate away from it. The distortion was found to be small overall, largest for the (100) surface, and smallest for the (111) surface. However, the parameters that were used in the potential functions were derived from bulk properties. The more recent theoretical work [29,30] indicates that parameters of this type can give completely erroneous results when applied to surfaces. Olander [23b] used the same potential functions, but his H-Cu parameters were not sensitive to variation of the first layer separation distance.

Andersson and Pendry [34] have concluded from a comparison of calculated and measured LEED intensity profiles that, if the Ni (100) surface is dilated, it is not dilated by more than 0.15 Å. Laramore [35] concluded from a similar study that the uppermost interlayer spacings of the Ni (100) and Ni (111) faces coincide with their bulk value to within ca. 0.1 Å. Laramore [36] has also analyzed LEED intensity profiles for Cu (100) and Cu (111). The best fit for Cu (100) was obtained when the upper-layer spacing equalled the bulk value. In the case of Cu (111) some features of the calculated curves agreed best with experiment when the upper-layer spacing equalled the bulk value whereas some features agreed best for a slightly contracted upper-layer spacing. He concluded that the upper-layer spacing of both faces equals the bulk value to within ca. 5%.

The most that can be said following this short review of the literature is that if the low index surfaces of fcc metals distort at all, the distortion is small, and, if a distortion occurs and it can be described simply as a change in the spacing between the top layer and the first sublayer, it is very likely that the distortion is a contraction. Accordingly, we have examined the effect on the H-Cu(s) bond of a 5-15%contraction in the first interlayer spacing of the Cu (100) and Cu (110) surfaces. In general, the bonds are weakly perturbed to an extent depending on the equilibrium adsorption distance. All the bonds except one grow stronger with the contraction, but a contraction of 15% results in a less than 10% increase in bond energy. The maximum bond energy site on the (110) surface is very slightly destabilized by the contraction. The H-Cu(s) potential is thus relatively insensitive to changes in the first layer separation distance of the order inferred from experiment and consequently the present treatment of the surface simply as a truncated bulk crystal seems to be well justified.

#### 3. The diatom-solid interaction potential

# 3.1. The dissociative adsorption model

In a classic paper [10] dealing with the adsorption and diffusion of gases on solid surfaces, LJ proposed a simple model to account for the relationship that had been observed between the amount of gas adsorbed by a metal and the temperature. The interaction between a molecule AB and a metal M is attributed to Van der Waals forces and represented by curve (a) in fig. 2. There is a small minimum at a large distance,  $R_p$ , from the metal. If the bonding between the individual groups A and B and the metal is greater than the energy required to dissociate the A-B bond, then the interaction of the two widely separated fragments with the metal may have the form of curve (b). The latter curve has a much larger minimum at a smaller distance and intersects the first curve at a point, C, which lies at an energy,  $E'_a$ , above that of the infinitely separated molecule-metal system. The energy  $E'_{a}$  can be interpreted as an energy of activation for a radiationless transition (or curve hopping) from state (a) to state (b), i.e., for dissociative adsorption. Thus, a molecule approaching the metal with an energy insufficient to reach C might tunnel through the barrier, but the probability is low unless its energy is very nearly equal to  $E'_{a}$ . If the energy of the impinging molecule is large, the molecule will move through the point C very quickly and the transition probability is again small. In this simple model, the transition is most likely to occur when the energy of the molecule and the activation energy are approximately equal. It follows that the probability of dissociative adsorption is small at low and high temperatures.



Fig. 2. The Lennard-Jones potential energy diagram for the dissociative adsorption of a molecule AB on a metal M [10].

# 3.2. The experimental situation

Copper is one of the few exceptions to the rule of thumb that metals adsorb hydrogen dissociatively without activation  $(E_a \leq 0)$  at low temperatures. Stickney and his coworkers recently used permeation [37] and molecular beam [38] techniques to study the adsorption and desorption of H<sub>2</sub> and HD from single crystal faces of copper. They concluded from their molecular beam results that the LJ model with a single energy barrier to dissociative adsorption is qualitatively, but not quantitatively satisfactory. Using a formula for the angular distribution of desorbed molecules that was derived recently [39] in this model, they calculated the following activation energies (kcal/mole): permeation study [37]:  $E_a(100) \approx$  $5, E_a(110) \approx 2, E_a(111) \approx 6$ ; molecular beam study [38]:  $E_a(100) \approx 5, E_a(110) \approx$ 3. They also suggest that the activation energies should be close to the maxima in the derivatives of their molecular beam adsorption probability curves and thereby obtain  $E_a(100) \approx 5$  and  $E_a(110) \approx 3$  kcal/mole [38].

Balooch and Stickney [37] (BS) found that the angular distributions of  $H_2$  desorbed from the low index faces of copper depend on the crystal orientation, but not on the azimuthal angle between the plane of detection and the principal axes of the surface lattice. They interpreted these observations tentatively in terms of a LJ model with the atomic and molecular interaction potentials crossing at a point sufficiently distant from the surface that (i) the variation with azimuthal angle is weak and (ii) the height of the barrier is determined by a small shift in the atomic potential relative to the less structure-sensitive molecular potential. They went no further, but it follows immediately from their second postulate that the bond energies on the low index faces must be in the reverse order to the barrier heights and thus in the order proposed in section 2.1. Conversely, it follows from this postulate and the bond energies calculated in section 2.2 that  $H_2$  chemisorption should proceed with less activation energy on the stepped (311) face than on the (110) face and its component (100) and (111) faces.

# 3.3. Calculations and results.

In order to calculate the diatom-solid interaction potential,  $\mathcal{U}_{AB}$ , we first assume that it can be expressed as a sum of interactions between the diatom AB and the individual solid atoms, i.e., as a sum of three-body potentials. We further assume that the admolecule atoms and the solid atoms can all be treated as oneelectron atoms. Then the *three-body* potential,  $U_i$ , between the diatom and *i*'th solid atom can be equated to the difference between a three-atom LEPS potential and the diatom singlet potential  ${}^{1}u_{AB}$ . We thus write

$$\mathcal{U}_{AB} = \sum_{i} U_{i} + {}^{1}u_{AB},$$

 $U_i = Q_{\mathrm{A}i} + Q_{\mathrm{B}i} + Q_{\mathrm{A}\mathrm{B}}$ 

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$$-2^{-1/2} [(\alpha_{Ai} - \alpha_{Bi})^{2} + (\alpha_{Ai} - \alpha_{AB})^{2} + (\alpha_{Bi} - \alpha_{AB})^{2}]^{1/2} - {}^{1}u_{AB},$$
  
$$Q_{kl} = \frac{1}{2} ({}^{1}u_{kl} + {}^{3}u_{kl}), \quad \alpha_{kl} = \frac{1}{2} ({}^{1}u_{kl} - {}^{3}u_{kl}), \qquad (2)$$

where  ${}^{1}u_{kl}$  and  ${}^{3}u_{kl}$  denote the potential curves for the lowest singlet and triplet states, respectively, of the diatom kl. These equations reduce to those for the pairwise additive model for adatom-solid interactions in the limit where the distance between the atoms of the admolecule is infinite. The zero of potential energy occurs when the admolecule atoms are infinitely separated from the surface as well as from one another. Accurate Morse and anti-Morse functions have been reported [40] for the lowest singlet and triplet states of H<sub>2</sub>, respectively. These functions are used in the present work. An anti-Morse function, which has the form

$${}^{3}u(r) = \frac{1}{2}{}^{3}u_{0} \left\{ \exp\left[-2{}^{3}\beta(r-r_{0})\right] + 2\exp\left[-{}^{3}\beta(r-r_{0})\right] \right\},$$
(3)

is also used to describe the lowest triplet pairwise H-Cu potential.

Using (1)—(3), we have calculated potential energy curves for various approaches of a hydrogen molecule towards the (100), (110), (111) and (311) faces of copper. The distance between the admolecule's center of mass (c.m.) and a chemisorption site is identified with the R of fig. 2. The same restrictions are placed on the approach of the admolecule's c.m. as were placed before on the approach of an adatom: it is restricted to lines normal to the surface or to the facets of a stepped surface. We varied R in increments of 0.1 Å. The admolecule's c.m. is taken to be



Fig. 3. The definition of the angles  $\phi$  and  $\theta$ .

the origin of a second set of Cartesian axes which are parallel to the solid-based axes when the direction of approach is normal to the surface. The orientation of the diatom is defined with respect to the molecule-based axes by the two angles  $(\phi, \theta)$ - see fig. 3. The H<sub>2</sub> internuclear distance was held fixed at the equilibrium distance observed for the ground state.

The activation energy for a particular site and approach is assumed to be determined by the point where the admolecule-solid potential curve crosses the potential curve for two infinitely separated adatoms moving towards maximum bond energy sites along maximum bond energy approaches. Using the same parameters in the potential functions for the lowest singlet and triplet pairwise H-Cu potentials, we obtained no physisorption and activation energies for the low index surfaces that are too high. As a consequence, we adjusted  ${}^{3}u_{0}$  and  ${}^{3}\beta$  so that the calculated minimum activation energy on the (110) surface agreed with the "observed" value [37,38], after substracting the zero-point energy (0.27 eV) of the H<sub>2</sub> molecule. We chose to parameterize against the (110) surface to ensure that the activation energy for this surface was calculated to be positive. The final parameter values are  ${}^{3}u_{0} =$  $0.6 {}^{1}u_{0}$ ,  ${}^{3}\beta = 1.5 {}^{1}\beta$ . Using these parameters, we calculated attractive H<sub>2</sub>-Cu(s) potential curves for the four surfaces under investigation and the correct order for the activation energies on the low index faces.

The results are summarized in table 4. As a consequence of varying R in increments of 0.1 Å, we are only able to place upper and lower limits on  $R_c$  and  $E'_{a}$ . These limits, however, generally determine  $R_{c}$  and  $E'_{a}$  with sufficient precision for our purposes. The maximum  $H_2$ -Cu(s) bond energies are in the order (311) > (110) > (111) > (100), similar in magnitude to the admolecule's zero-point energy, and relatively insensitive to the nature of the surface. They are probably too high by a factor of 2. The following minimum activation energies (kcal/mole) are calculated:  $E_a(100) \simeq 11$ ,  $E_a(110) \simeq 2$ ,  $E_a(111) \simeq 16$ ,  $E_a(311) = 0$ . Once again the calculated values of  $E_a(100)$  and  $E_a(111)$  are too high compared to the "observed" values, but  $E_a(111) - E_a(100)$  is correctly predicted to be ca.  $0.5 \times$  $[E_a(100) - E_a(110)]$ . The maximum H<sub>2</sub>-Cu(s) bond energies and minimum activation energies are obtained for the same admolecule approaches. The activation energy is generally higher when the  $H_2$  molecule is oriented so that it is perpendicular to the surface (or facet). Approaches towards sites located at the bottom of the step on the (311) surface are for steric reasons mainly responsible for the few exceptions to this rule. As in the case of the adatom-solid potential, the admolecule-solid potential is more uniform for the (111) surface than for the other surfaces.

The H-Cu(s) and H<sub>2</sub>-Cu(s) curves cross at distances from the low index faces that seem shorter than those that might be considered to be consistent with the BS model. Consequently, it might not be a good approximation to keep the internuclear separation of the H<sub>2</sub> molecule fixed at its equilibrium value in the ground state of the isolated molecule. Nevertheless, the calculated H<sub>2</sub>-Cu(s) potential for the low index faces is only weakly dependent on the azimuthal angle  $\phi$  in the cross-

#### Table 4

 $H_2$ -Cu(s) bond energy,  $E_p(eV)$ , bond distance,  $R_p(A)$ , activation energy,  $E'_3(eV)$ , and  $R_c(A)$ as a function of surface, site and approach; the minimum activation energy calculated for each surface is underlined; the site coordinate y increases down the tables

Site	φ	θ	Rp	Ep	R <sub>c</sub>	E'a
(100)						
1	0	0	2.8	0.1995	1.8 - 1.9	1.167-1.377
1	0	90	3.1	0.1665	2.0 - 2.1	1.595-1.815
2	0	0	2.7	0.2139	1.7 - 1.8	0.970-1.167
2	90	0	2.7	0.2243	1.6 - 1.7	0.850-0.970
2	0	90	2.9	0.1895	1.8 - 1.9	1.167-1.303
3	0	0	2.6	0.2405	1.57–1.58	0.75-0.76
3	0	90	2.7	0.2150	1.6–1.7	0.793-0.848
(110)						
1	0	0 <sup>.</sup>	2.9	0.1585	1.8-1.9	1.685-1.795
1	90	0	2.9	0.1594	1.8-1.9	1.685-1.768
1	0	90	3.1	0.1311	1.9-2.0	2.108-2.134
2	0	0	2.8	0.1705	1.6-1.7	1.407-1.452
2	90	0	2.7	0.1796	1.6-1.7	1.216-1.301
2	0	90	3.0	0.1496	1.7-1.8	1.452-1.685
3	0	0	2.3	0.2446	1.2–1.3	0.491-0.521
3	90	0	2.4	0.2215	1.4–1.5	0.746-0.827
3	0	90	2.5	0.2107	1.3–1.4	0.644-0.746
4	0	0	2.2	0.2629	1.22-1.23	0.36
4	90	0	2.3	0.2506	1.2-1.3	0.391-0.521
4	0	90	2.3	0.2399	1.2-1.3	0.402-0.521
(111)						
1	30	0	2.8	0.2228	1.8-1.9	1.096-1.228
1	120	0	2.8	0.2228	1.8-1.9	1.096-1.228
1	0	90	3.1	0.1864	2.0-2.1	1.406-1.603
2	0	0	2.7	0.2355	1.7–1.8	$\begin{array}{r} 0.972 - 1.079 \\ 0.969 - 0.972 \\ \hline 1.079 - 1.228 \end{array}$
2	90	0	2.7	0.2427	1.6–1.7	
2	0	90	2.9	0.2078	1.8–1.9	
3	30	0	2.7	0.2419	1.71	0.98
3	120	0	2.7	0.2419	1.7–1.8	0.972-1.021
3	0	90	2.9	0.2115	1.8–1.9	1.079-1.104
4	30	0	2.7	0.2427	1.6-1.7	$\frac{0.969 - 0.972}{0.972 - 1.079}$ $1.079 - 1.228$
4	120	0	2.7	0.2355	1.7-1.8	
4	0	90	2.9	0.2078	1.8-1.9	
5	30	0	2.7	0.2419	1.7–1.8	0.972-1.021
5	120	0	2.7	0.2419	1.7–1.8	0.972-1.021
5	0	90	2.9	0.2114	1.8–1.9	1.079-1.104

Site	φ	θ	Rp	Ep	R <sub>c</sub>	$E'_{\mathbf{a}}$
(311)						
⊥(311)						
1	0	0	2.9	0.1471	2.0-2.1	0.700-0.722
1	90	0	2.9	0.1477	2.0 - 2.1	0.700-0.706
1	0	90	3.1	0.1211	2.1-2.2	0.919-1.141
2	0	0	2.8	0.1582	1.9-2.0	0.487-0.599
2	90	0	2.7	0.1661	1.8-1.9	0.355-0.487
2	0	<b>9</b> 0	3.0	0.1388	1.9-2.0	0.638-0.700
3'	0	0	3.1	0.1868	2.1-2.2	0.919-0.924
3'	90	0	3.2	0.1794	2.1-2.2	0.942-1.141
3'	0	90	3.4	0.1568	2.2 - 2.3	1.141-1.360
4'	0	0	3.0	0.2019	1.9-2.0	0.671-0.700
4'	<b>9</b> 0	0	3.0	0.2036	1.9-2.0	0.621-0.700
4'	0	90	3.2	0.1810	2.0 - 2.1	0.700-0.794
3	0	0	2.0	0.2838	1.5-1.6	<u>-0.165</u> to <u>-0.205</u>
3	90	0	2.1	0.2588	1.5-1.6	-0.068 to -0.125
3	0	90	2.2	0.2525	1.5-1.6	-0.068 to 0.100
4	0	0	2.0	0.2828	1.5-1.6	<u>-0.165</u> to <u>-0.205</u>
4	<b>9</b> 0	0	2.1	0.2588	1.5 - 1.6	-0.068 to -0.125
4	0	90	2.2	0.2525	1.5-1.6	-0.068 to 0.100
5'	0	0	3.1	0.2780	2.0 - 2.1	0.700-0.919
5'	90	0	3.2	0.2580	2.1-2.2	0.919-0.965
5'	0	90	3.3	0.2483	2.1-2.2	1.074-1.141
6'	0	0	3.1	0.2723	2.0 - 2.1	0.700-0.870
6'	90	0	3.3	0.2479	2.1-2.2	0.919-1.064
6'	0	90	3.3	0.2406	2.1–2.2	0.919-0.925
3″	0	0	3.2	0.1985	2.1-2.2	0.919-1.141
3″	90	0	3.3	0.1890	2.2-2.3	1.141-1.360
3''	0	90	3.5	0.1677	2.2-2.3	1.254-1.360
4"	0	0	3.2	0.1799	2.1-2.2	0.919-1.141
4"	90	0	3.2	0.1787	2.1-2.2	0.919-1.141
4″	0	90	3.4	0.1544	2.1 - 2.2	0.919-1.141
6″	0	0	3.2	0.1799	2.1-2.2	0.919-1.141
6"	90	0	3.2	0.1787	2.1-2.2	0.919-1.141
6″	0	90	3,4	0.1543	2.1-2.2	0.919-1.141
5″	0	0	3.1	0.1703	2.0 - 2.1	0.737-0.919
5″	90	0	3.0	0.1769	2.0-2.1	0.700-0.800
5"	0	90	3.2	0.1502	2.1 - 2.2	0.919-1.046
(311)						
⊥(100)						
1'	0	0	2.9	0.1918	1.9-2.0	0.683-0.700
1'	90	Ō	2.9	0.1933	1.9-2.0	0.674-0.700
1'	0	90	3.1	0.1626	2.1-2.2	0.919-1.141

Site	φ	θ	Rp	Ep	R <sub>c</sub>	E'a
2'	0	0	2.8	0.2039	1.9-2.0	0.487-0.561
2' 2'	90 0	0 90	2.7 3.0	0.2128 0.1814	1.8-1.9 1.9-2.0	0.321-0.487 0.599-0.700
3'	0	0	2.8	0 2746	18-19	0 286-0 487
3'	90	Ő	3.0	0.2405	1.9-2.0	0.487-0.594
3'	0	90	3.0	0.2510	1.9 - 2.0	0.546-0.700
4'	0	0	2.8	0.2661	1.7 - 1.8	0.252-0.284
4'	90	0	3.1	0.2087	1.8-1.9	0.284-0.434
4'	0	90	2.9	0.2433	1.8-1.9	0.284-0.421
5'	0	0	4.3	0.1585	2.7-2.8	2.183-2.368
5'	90	0	4.3	0.1594	2.7-2.8	2.183-2.368
5'	0	90	4.4	0.1428	2.6-2.7	2.067-2.183
6'	0	0	4.4	0.1472	2.9-3.0	2.544-2.711
6'	90	0	4.5	0.1412	3.0-3.1	2.791-2.868
6'	0	90	4.6	0.1247	3.1-3.2	2.868-2.876
(311) 1(111)						
1	0	0	2.9	0.2102	1.9-2.0	0.678-0.700
1	90	0	2.9	0.2115	1.9-2.0	0.669-0.700
1	0	90	3.1	0.1802	2.1-2.2	0.919-1.141
2	0	0	2.8	0.2211	1.9-2.0	0.487-0.571
2	90	0	2.8	0.2273	1.8-1.9	0.351-0.487
2	0	90	3.0	0.1976	1.9 - 2.0	0.615 - 0.700
1″	0	0	4.6	0.1471	2.9-3.0	2.544-2.711
1″	90	0	4.7	0.1394	3.1-3.2	2.868-3.017
1"	0	90	4.8	0.1262	3.0-3.1	2.711-2.868
2″	0	0	4.5	0.1583	2.6-2.7	2.078-2.183
2″	90	0	4.5	0.1573	2.7-2.8	2.183-2.368
2″	0	90	4.6	0.1447	2.5-2.6	1.786-1.870
3″	0	0	3.5	0.2053	1.9-2.0	0.487-0.571
3″	90	0	3.7	0.1797	1.9-2.0	0.549-0.700
3"	0	90	3.4	0.2039	1.9-2.0	0.605-0.700
4"	0	0	2.9	0.2668	1.8-1.9	0.412-0.487
4″	90	0	3.2	0.2115	1.9 - 2.0	0.487-0.618
4″	0	90	3.0	0.2453	1.9-2.0	0.611-0.700
6"	0	0	2.9	0.2668	1.8-1.9	0.412-0.487
6"	90	0	3.2	0.2115	1.9-2.0	0.487-0.618
6″	0	90	3.0	0.2453	1.9-2.0	0.611-0.700
5"	0	0	2.8	0.2810	1.8-1.9	0.361-0.487
5"	90	0	2.8	0.2536	1.8-1.9	0.398-0.487
5″	0	90	2.9	0.2526	1.9 - 2.0	0.487 - 0.700

Table 4 (continued)

ing region and is therefore consistent with BS's first postulate. The (110) surface is the roughest of the three and shows the greatest asymmetry. Furthermore, the activation energy distributions for the low index faces can be understood simply in term of BS's second postulate.

As expected on the basis of this postulate and the atom-solid results, the effect of the steps on the (311) surface is to give activation energies for approaches towards most of the sites on its two facets, along paths normal to the facet in question, lower than those for the analogous interaction paths on the component low index faces. [The exceptions are the edge sites (for bond energy reasons) and the sites located at the bottom of the step (for steric reasons).] However, only in one case (site 4',  $\theta = \phi = 0$ ) does such an approach correspond to an  $E_a \simeq 0$ .

The unexpected feature of our results is that the lowest activation energies for the (311) surface are obtained when the H<sub>2</sub> molecule approaches sites above the (100) facet on the uppermost (311) plane not vary far from the projection of the bottom of the step on that plane (sites 3 and 4), along paths normal to the (311) face. Dissociative adsorption is predicted to occur without activation at these sites. However, the variation of  $E_a$  with the y-coordinate of the site is quite marked in their neighborhood. The activation energies for the edge sites are also lower than expected. In thus appears that the second BS postulate is able to explain the main trend in the calculated activation energy distribution for the (311) face, but not the details of the distribution. Alternatively, the distribution might be skewed by the choice of the reference atom—solid potential.

The basic picture of  $H_2/Cu(311)$  chemisorption which emerges from the calculations agrees with a note added in proof to ref. [18] that equilibrium  $H_2$  adsorption on Cu(311) resembles Cu(110) [rather than Cu(100) or Cu(111)].

# 3.4. Discussion

The dissociative adsorption of hydrogen on metals has been studied previously by EH methods [2b,d] with limited success. The reaction paths explored in these studies leads to two hydrogen atoms bonded to *adjacent* sites on the substrate. However, the well known failure of single configuration MO methods to describe the dissociation limit of covalent bonds largely restricts their applicability to "chemical" geometries. Consequently, adatom—solid interaction potentials are only calculated at ordinary bonding distances and the bond energy is equated to the difference between the energy of the combined system and the total energy of the separated adatom and metal cluster. Another well known short-coming of EH methods is that they exaggerate charge transfer between neighboring heteroatoms. Baetzold [2d] also noted that, because such calculations have been restricted to small metal clusters, it is likely that they are more valid for chemisorption on supported metal crystallites than on semi-infinite single crystal surfaces. In the perturbation studies [6a,b], the solid was modelled by just two metal atoms.

The present model for dissociative adsorption of H<sub>2</sub> on copper suffers from none

of these drawbacks. Results that are negligibly different from the fully converged ones are readily computed. On the other hand, the diatom—solid interaction potential is calculated using valence bond theory. This imposes homopolarity on the chemisorption bond and consequently the present approach is unsatisfactory to the extent that the bond is ionic. An interesting point is that the first order interaction energy calculated in the perturbation studies [6a,b] equals the result of a valence bond calculations and in those studies the three-body interactions were found to be both qualitatively and quantitatively important.

Balooch et al. [38] have noted a possible difficulty with the Lennard-Jones model. The H<sub>2</sub> interatomic distance (0.74 Å) is much smaller than that of the copper atoms on, say, the (100) surface (2.5 Å). Thus, an H<sub>2</sub> molecule incident upon site 3 on this surface may not experience an attractive force tending to pull it apart, in which case dissociation is unlikely. On the other hand, an H<sub>2</sub> molecule incident upon site 2 will "see" potential minima on either side of the site and thus experience the force necessary to dissociate it. The results of recent empirical potential surface calculations support this view [21b]. Hence, the assumption that no further work is required to dissociate the molecule in a direction parallel to the surface at the points where the calculated atom-solid and diatom-solid potential curves cross may not always be true. This will not be clear, however, until the Lennard-Jones model is abandoned and the H<sub>2</sub> internuclear distance is allowed to relax. This will be necessary in any event before more accurate estimates of the activation energies can be made and before classical trajectory calculations of the reaction dynamics can be carried out.

A theoretical investigation of chemisorption of  $H_2$  on W(100) that is similar in some ways to the present study has been reported by McCreery and Wolken [8]. They formulated the interaction of a diatomic molecule with a surface as a single, simplified, four-atom LEPS potential. The parameters of the functions used to represent the H-W pairwise potentials were obtained by fitting them to the results of an extended Hückel MO calculation for the H-W(100) system. The surface was approximated by a static background potential, periodic in the plane of the surface. McCreery and Wolken have used their  $H_2$ -W(100) model potential to carry out classical trajectory studies of the reaction dynamics [41].

The present model ascribes much greater activity to the stepped Cu(311) face than to either of its two component faces separately. The extent to which steps enhance the dissociative adsorption of  $H_2$  on platinum has been investigated recently in a number of laboratories. Lang et al. [42], concluded from LEED studies that at room temperature hydrogen does not chemisorb easily on the (100) or (111) faces of platinum, but chemisorbs readily on platinum (111) faces with (111) steps. Subsequently, Bernasek et al. [43], carried out a molecular beam study of hydrogen-deuterium exchange on platinum single crystal faces. Since the reaction product, HD, was detectable from Pt(111) surfaces with (111), steps, but not from the Pt(111) face itself, it was concluded that steps play a controlling role in the reaction. These conclusions are not consistent, however, with a series of reports from other laboratories that hydrogen dissociatively adsorbs on the (100) and (111) faces of platinum [44,45] and that stepped surfaces similar or identical to those studied by Somorjai and his coworkers are not more active than expected on the basis of differences in sticking coefficients [45,46]. In addition, the beam data [43] were reinterpreted recently in terms of an alternative mechanism which represents the data more accurately and leads to a similar conclusion about step enhancement of activity [47]. Nevertheless, the influence of steps on the kinetics of H<sub>2</sub> interaction with Pt(111) is still marked enough to cause appreciable effects on the rates and selectivities of catalytic reactions involving adsorbed hydrogen [46]. Chemisorption on the Pt(100) face is complicated by surface reconstruction. Both H<sub>2</sub> and O<sub>2</sub> readily chemisorb on the unreconstructed surface at room temperature, but not on the reconstructed surface [48].

# 4. Conclusion

The principal result of the present study of the dissociative adsorption of  $H_2$  on copper is the prediction that this process should proceed on the stepped (311) face with much greater ease than on either of its two component (100) and (111) faces separately. Instead, the *thermochemistry* of chemisorption on the (311) face is expected to resemble that of the (110) face. Experimental data already in the literature were used to make a strong case that the heats of adsorption of  $H_2$  on the low index faces are in the order (110) > (100) > (111). The heats of adsorption calculated with this constraint and two others, also imposed by experiment, are:  $\Delta H_a (100) = -3$ ,  $\Delta H_a (110) = 12$ ,  $\Delta H_a (11) = -15$  kcal/mole.

The activation energy distributions calculated for the low index faces can be understood in terms of a LJ model proposed by Balooch and Stickney [37] in which the height of the barrier is determined by small shifts of the atomic potential relative to the molecular potential. This simple model, however, is not completely satisfactory for the (311) face.

H-Cu(s) bond energies for the low index faces are predicted to increase with the adatom's local coordination number. The least preferred sites on the (311) face are the edge sites. Our results are generally supportive of the reason advanced by Lang et al. [42], for the enhanced activity of stepped platinum surfaces. They argued that a molecule adsorbed at (a notch of [2b]) a step has a greater number of nearest neighbors than a molecule adsorbed at a flat surface and, therefore, access to a greater number of metal atom orbitals. However, the present results for the chemisorption of hydrogen on copper are not expected to apply to the chemisorption of hydrogen on metals like platinum where the directed character of metal p and/or d orbitals is important. This has not yet been established for nickel. However, the recently measured heats of adsorption of H<sub>2</sub> on the low index faces of nickel [24a-d] are not explained satisfactorily by the pairwise additive model

and a LJ interatomic potential. Nevertheless, the applicability of the pairwise additive model itself cannot be ruled out entirely until it has been used in conjunction with more flexible interatomic potentials like the Morse potential.

Balooch et al. [38], also reported an activation energy of 5 kcal/mole for the dissociative adsorption of  $H_2$  on the Cu(310) surface. This surface is a stepped one consisting of (100) terraces three atomic rows wide, separated by (110) steps, one atomic layer high. Both the energy dependence for dissociative adsorption and the angular distribution of desorbed HD for this surface were found to be essentially the same as those for the (100) surface and quite different from those for the (110) surface. This implies that the role of the (110) steps on the (310) face, unlike that predicted for the steps on the (311) face, is not important in the chemisorption of  $H_2$ . Since the (310) face has both a lower step density *and* a lower atom density than the (311) face, these factors may be the controlling ones for step enhancement of the activity of copper. Calculations are currently underway to determine if the present model predicts the behavior observed for the (310) face.

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# Appendix

We will compute the interaction of the adatom with the remainder of the semiinfinite solid (which was neglected in section 2). The computation will be done by a continuum method:

$$\Delta E = \sum_{i}' u(\mathbf{r}_{ai}) = \int \rho(\mathbf{r}_{i}) u(\mathbf{r}_{ai}) \,\mathrm{d}\mathbf{r}_{i}.$$

 $\rho(r_i)$  is the density function of copper atoms in the bulk. This will be taken to be  $1/v = 1/a_0^3$  where  $a_0$  is the nearest neighbor distance in bulk copper. Then, since  $r_{ai}$  is large for all these atoms, we need only consider the attractive part of the potential. Rather than use the Morse potential, we will use a Lennard-Jones (LJ) potential which will overestimate  $\Delta E$  since the LJ falls off more slowly than the Morse for large distances. Thus,

$$|\Delta E| < \frac{1}{a_0^3} \int \frac{|c|}{r^6} dr = \frac{2\pi}{a_0^3} \int_{\rho_0}^{\infty} d\rho \rho \int_{z_0}^{z_f} dz \frac{|c|}{(\rho^2 + z^2)^3},$$

where c is the attractive parameter in the LJ potential and where we have approximated the shape of the region by a cylinder (instead of a rectangular parallelpiped). The limits on the integration are such as to remove from a semi-infinite solid a cylinder of height  $z_f - z_0$  ( $z_0$  is the height of the adatom above the surface) and radius  $\rho_0$ . Thus,

$$|\Delta E| < \frac{2\pi |c|}{a_0^3} \left[ \int_{z_0}^{z_{\rm f}} \mathrm{d}z \int_{\rho_0}^{\infty} \mathrm{d}\rho \,\rho(\rho^2 + z^2)^{-3} + \int_{z_{\rm f}}^{\infty} \mathrm{d}z \int_{0}^{\infty} \mathrm{d}\rho \,\rho(\rho^2 + z^2)^{-3} \right],$$

or

$$|\Delta E| < \frac{2\pi |c|}{a_0^3} \left[ \frac{(z_{\rm f} - z_0)}{4(\rho_0^2 + z_0^2)^2} + \frac{1}{12z_{\rm f}^3} \right]$$

In the last equation, we have put an upper bound on the first integral by replacing z by  $z_0$ . Since  $z_0 \ll z_f$  and  $\rho_0$ , we find

$$|\Delta E| < \frac{\pi |c|}{2a_0^3} \left( \frac{z_{\rm f}}{\rho_0^4} + \frac{1}{3z_{\rm f}^3} \right).$$

We approximate |c| by setting the LJ potential equal to our Morse potential (see table 1) at the minimum,  $R_0$ . This will give a much larger attraction (and hence |c|) than is possessed by the Morse potential. We find  $|c| = 2U_0R_0^6$ ; therefore, we have

$$|\Delta E| < \frac{\pi U_0 R_0^6}{v} \left( \frac{z_f}{\rho_0^4} + \frac{1}{3z_f^3} \right).$$

In the case of H–Cu(s), we have  $R_0 = 2.3$  Å,  $z_f \ge 8$  Å,  $\rho_0 \cong 10$  Å, and  $a_0^3 \cong 12$  Å<sup>3</sup> so that

 $|\Delta E| < \frac{1}{16} U_0 = 0.02 \text{ eV} = 0.5 \text{ kcal/mole}$ .

Thus, by neglecting the remainder of the crystal, there is a maximum error of 0.5 kcal/mole in our estimate of the H-Cu(s) bond energy.

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