

## INDIRECT INTERACTIONS OF H/Ni(111) AND H/Pd(100) USING EMBEDDED ATOM METHOD

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Using the embedded atom method (EAM), we computed lateral interactions between H atoms on Ni(111) and on Pd(100). For H/Ni(111) the binding-energy difference between the two 3-fold sites is very small. As expected due to the very small separation, at nearest neighbor sites there is an extreme repulsion. The only other non-negligible interactions are repulsions of comparable size (a few meV) between H pairs at 2nd and 3rd neighbor separations. Energies for ordered patterns are consistent with isolated pairs: multi-site effects are not significant. Zero-point motion weakens the repulsions for isolated pairs but not for ordered overlayers. Local relaxations are minor. There are no anomalous attractions, but interactions are much smaller than expected from experiment, and  $(2 \times 1)$  ordering is predicted instead of the observed graphitic  $(2 \times 2)$ . Recent extensions of EAM suggest ways to compute more reliable magnitudes. For H/Pd(100) adsorption is predicted in center sites, but slightly below the surface plane rather than above. The interactions have realistic signs and orders of magnitude, but  $(2 \times 1)$  ordering is predicted rather than the observed  $c(2 \times 2)$ .

### 1. Introduction

Among the severest challenges in calculations of total energies is the lateral interaction energies of atoms chemisorbed on transition metal surfaces [1]. The low symmetry of the problem limits self-consistent total energy techniques to high-density ordered overlayers; it is thus difficult or impossible to compute any but the shortest-range interactions. Thus, progress beyond the crude models of indirect interactions presented nearly two decades ago has been rather limited [1]. To the extent that a lattice-gas picture is appropriate, it is these interactions which determine the 2D temperature–coverage phase diagram. In principle, then, one can deduce these interactions by treating them as fitting parameters to be adjusted to reproduce the experimental phase diagram [2]. However, there are severe problems due to (1) lack of uniqueness, (2) an enormous range of possible parameters, and (3) the experimental difficulties in achieving (a) cryogenic temperatures and, more signifi-

cantly, (b) equilibration to obtain the low-temperature data that can often discriminate among qualitatively different sets of interactions. It is thus desirable to have a reasonably reliable starting set of interactions that can be fine-tuned. Conversely, given a set of predicted interactions, comparison of the consequent phase diagram with experiment offers a stern test [3].

Most theoretical progress in studying covalent adsorption has focused on hydrogen as the adsorbate, due to the obvious simplicity of its electronic structure as well as its abundance and technological importance. In particular, many of its properties in and on metals have been studied first by Muscat using an embedded cluster technique [4,5] and more recently by the family of effective medium theory [6], quasi-atom [7], and embedded atom method [8]. The effective medium theory (EMT) has been applied successfully to chemisorption [9–11], vibrational modes [10,11], and diffusion of hydrogen on metal surfaces [10]. The embedded atom method (EAM) has also been

applied to hydrogen chemisorption [8,12,13] and hydrogen diffusion [14]; for H adsorbed on Pd(111) [13], good agreement was obtained between the theoretical and experimental phase diagrams.

In this short paper we describe the application of the embedded atom method (EAM) to H on Ni(111) [12], as well as a brief study of H on Pd(100) [13]. We find that the interactions generally are repulsive and have the correct *sign* to be consistent with the experimental H/Ni(111) phase diagram [15]. The *ratios* do not always give the correct ordered phases. The decay with increasing adatom separation is extremely rapid once the adatoms no longer share a common substrate atom as a nearest neighbor. For Ni, the interactions are an order of magnitude smaller than are needed to account, in a lattice gas picture, for the transition temperature of the graphitic ( $2 \times 2$ ) [or ( $2 \times 2$ )-2H] overlayer. The general, semiquantitative features of our results do not depend on how the semi-empirical EAM functions were determined. However, from results [16] appearing after the completion of these calculations, it seems that by generalizing the EAM procedure one can obtain interactions for H/Ni(111) that have the expected order of magnitude.

## 2. H/Ni(111)

### 2.1. Computational details and single-adatom results

Three sets of semi-empirical functions were used in these calculations. The first two sets started with the functions for pure Ni from ref. [17]. The hydrogen functions and the H–Ni interaction were then determined by fitting to the solution energy and the migration energy of hydrogen in bulk nickel, the chemisorption energy at the 4-fold center site of the (100) surface and at the 3-fold center site on the (111) surface, the equilibrium height of the hydrogen above the (100) surface, and by requiring that the calculated “classical” energies (i.e. neglecting zero-point motion) reproduced the observed adsorption sites on the (100), (110), and (111) surfaces. The parametrized functions reported in ref. [12] (“set 1”) were based on

equal weighting of the properties on the different surfaces. The second set differed only in that, during optimization, more weight was given to the properties on the (100) surface [18]. The third set was based entirely on fitting to bulk properties (including hydrogen impurities in the bulk); the EAM functions are listed explicitly in ref. [8]. Interactions computed using this older set generally fell between those calculated using the first two sets. Zero-point corrections were calculated in the harmonic approximation, as in ref. [13].

For the calculations of the H/Ni(111) system, we used a Ni slab nine layers thick, with the bottom three layers fixed in their bulk positions. Periodic boundary conditions were invoked in the two directions parallel to the surface. When looking at two or three hydrogens on the surface, we took a large enough slab (36 atoms per layer) that no significant spurious interactions were added by the boundary conditions. Hydrogen is believed to occupy both kinds of 3-fold sites, fcc-like (above the third layer of the substrate) and hcp-like (above the second layer) [15,19]. By construction of the functions [12], the “classical” adsorption energy of a single hydrogen atom is 2.847 eV. The zero-point contribution is usually thought not to alter lateral interactions significantly; for ordered overlayers, our work is consistent with this belief, but for isolated H pairs the zero-point contribution is notable. These vibrational effects were checked on a thinner substrate, seven layers thick, 16 atoms per layer; the change in “classical” values from the larger substrate were insignificant. Fixing or releasing the last three layers also had no significant effect [20].

The binding energy difference between the two kinds of 3-fold sites is insignificant, as in experiment [19]. (With the first set of functions, there is a 0.4 meV preference for fcc sites; with the second or third sets, the hcp site is preferred by 1/2 or 1 meV, respectively.) There is no evidence of adsorption in the subsurface sites which play an important role in H/Pd(111) [13] [and possibly H/Ru(0001) [22]]. As reported earlier [12], zero-point motion decreases the binding energy of one H by 0.13 eV; it also reverses the marginal preference of set 1 to favor hcp sites, by 0.4 meV. To repeat, though, the overriding result is that H will

adsorb in both types of 3-fold types with comparable probability at temperatures relevant to experiments. The differences between values, on the order of a fraction of an meV, provide a gauge of the uncertainties in *absolute* numbers in EAM.

## 2.2. Lateral interactions

In our calculations, interactions more widely spaced than third neighbor were tiny, of order 0.1 meV or less. This underestimate of long-range interaction, compared to expectations for real systems [1], seems intrinsic to the approximation of superposition of atomic orbitals [1,13,21]. It is singularities related to the Fermi surface which determine the asymptotic form of the interaction [1,23]. As in an EAM study of H/Pd(111) [13], the significant pair interactions involve those configurations in which the adatoms share a nearest neighbor in the substrate, viz.  $w_1$ ,  $w_2$ , and  $w_3$ , where  $w_n$  denotes the  $n$ th-neighbor pair interaction. (See fig. 1a.) With set 1 the “classical” values of  $w_2$  and  $w_3$  are both about +3 meV, i.e. very small repulsions with comparable size [24]. (Note that  $w_2$  with both adatoms in hcp sites is less than

$w_2$  with both H’s in fcc sites by an insignificant amount: 0.1 meV.) For H/Pd(111) these repulsions were more than an order of magnitude larger, in the range 70–110 meV [13]. In the EAM perspective, the repulsions arise from the positive curvature of the embedding function; this curvature is much larger for H in Pd than in Ni. Also,  $w_3$  is comparable to  $w_2$  because both involve a single common substrate nearest neighbor. (On the other hand, the  $w_1$  bond, which involves two common substrate neighbors, is at least an order of magnitude larger, rather than just twice as large: the shorter spacing of Ni than Pd brings the direct interaction strongly into play, overwhelming the *indirect* interaction and so overriding the trend of ratios characteristic of EAM).

Since  $w_2 < \frac{3}{2}w_3$  in EAM, a  $(2 \times 1)$  is favored [25] over the observed graphitic  $(2 \times 2)$  when half the sites are occupied (i.e. one H per two surface Ni’s). (Fig. 1b depicts the two patterns.) These numbers are somewhat similar to those produced by Muscat for  $w_2$ , but he found a stronger, attractive  $w_3$  [4,5a]. (Cf. table 1.) The only reason he obtained reasonable agreement with experiment for the disordering temperature of a complete

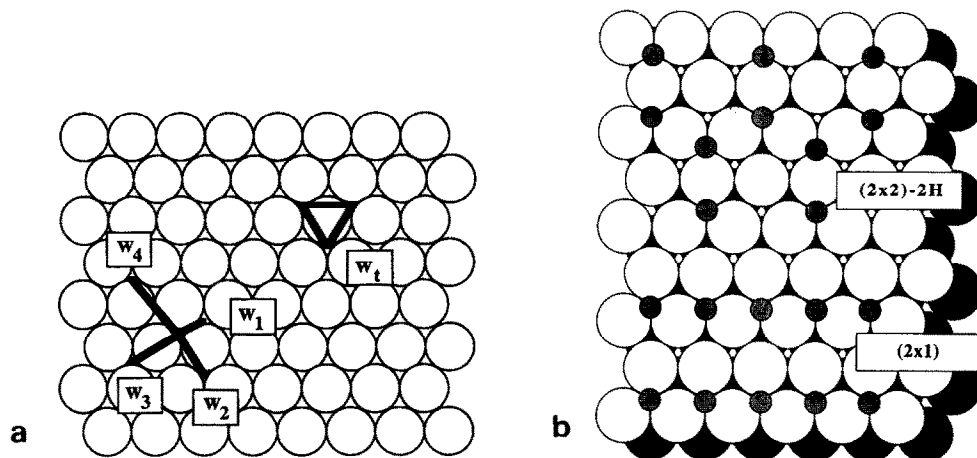


Fig. 1. (a) Schematic of a close-packed face illustrating  $n$ th neighbor separations (labeled by the corresponding energy  $w_n$ ). In EAM only  $w_1$ ,  $w_2$ , and  $w_3$  are significant for H/Ni(111); all are repulsions, with  $w_1$  essentially an exclusion. For  $w_2$ , both H’s are in the same type of 3-fold site; its value is essentially the same in either case. The trio interaction  $w_T$  is a weak, insignificant attraction. (b) Schematic of H/Ni(111) illustrating the two types of 3-fold binding sites (“hcp”, above a second-layer Ni [in black], and “fcc”, seen as downward-pointing triangles with a small, hexagon-like white spots). In EAM and in experiment [19], the adsorption energy is nearly the same for hcp and fcc sites. Also illustrated are the two ordered overlayers of H (depicted by smaller shaded circles). Above is the graphitic  $(2 \times 2)$ , or  $(2 \times 2)$ -2H, with lateral energy per H of  $\frac{3}{2}w_3$ , which is observed experimentally [15]. Below is the  $(2 \times 1)$ , with lateral energy per H of  $w_2$ , which EAM predicts to be the stable pattern.

Table 1  
Summary of lateral interactions  $w_n$  for H/Ni(111)

No. of shared Ni neighbors:	$w_1$ 2	$w_2$ 1	$w_3$ 1	$w_4$ 0	$w_T$
EAM, classical					
isolated pairs	+29	+3	+3	$\ll 1$	-0.8
ordered overlayer		+3 <sup>+</sup>	+3 <sup>+</sup>		
Zero-point, isolated pairs		-1.2	-0.4		
Quantum (classical + zero-point)					
isolated pairs		+1.5	+2.4		
ordered overlayer		+3.8	+3.0		
Muscat [5a], large symmetric clusters	[~ 400]	+3 ± 3	-6 ± 1	+0.6	
Muscat [4], isolated pairs	[450]	-2 ± 4	-10 ± 2		
EDIM (TTG) [16], isolated pairs		+43.9	+22.6	+3.5	
Roelofs et al. [3] (units of $w_2$ )	$\infty$	1	0.2	0.2	0

Energies are in meV. Configurations for each  $w_n$  are depicted in fig. 1a. EAM values are computed with Set 1.

graphitic ( $2 \times 2$ ) is because he deduced [5a] a  $w_6$  attraction which seems unrealistically large. Such an attraction would also produce broad coexistence regions of graphitic ( $2 \times 2$ ) and ( $1 \times 1$ ) [3], which conflict with experimental results [15]. It is also noteworthy that Muscat's [5b] interactions for H/Pd(111), deducible from the energy of several clusters, are only a factor of 2–3 as large in size as for H/Ni(111), with  $w_3$  again attractive.

Calculations for various ordered overlayers showed that they were well interpreted, within the accuracy of these calculations, by pairwise interactions: the ( $2 \times 1$ ) and the ( $2 \times 2$ )-2H could be described simply by repulsive  $w_2$  and  $w_3$ , respectively, of slightly above 3 meV. The slight ( $\leq 0.5$  meV) increase for the ordered overlayer may be due to the elimination, by symmetry, of the small lateral distortions of about  $0.017 \text{ \AA}$  that occur for isolated pairs. Test calculations with pairs of H's fixed in parallel coordinates but allowed to move vertically showed changes of +0.2 meV. The trio interaction (3 adatoms, pairs subtracted)  $w_T$  for an equilateral triangle of second neighbors ( $w_2$  pairs) was rather insignificant: -0.8 meV (smaller in magnitude and also attractive with sets 2 and 3). Since trio configurations with larger separations will not share a common substrate atom, an EAM estimate of their trio interaction should

be negligibly small. The energies of p( $2 \times 2$ ) [or ( $2 \times 2$ )-1H] overlayers in either fcc or hcp sites were adequately given by just the single adatom energy, corroborating the insignificance of pairwise interactions  $w_4$  and beyond.

The EAM has been quite successful in analyzing vibrational frequencies at the surface [26]. For a single H adsorbate, the zero-point energies associated with all vibrations in the cluster increase the total adsorption energy (i.e. decrease the binding energy) by nearly 130 meV, in general agreement with experiment and other calculations [27]. For the significant lateral interactions between isolated pairs, the vibrational effects were attractive: including zero-point motion decreased the repulsive  $w_2$  and  $w_3$  interactions, by 1.2 and 0.4 meV, respectively, to +1.5 and 2.4 meV. For ordered overlayers, zero-point motion does not change energies substantially: looking at the ( $2 \times 1$ ) in terms of  $w_2$  bonds, we found  $w_2$  is raised somewhat to 3.8 meV. For the ( $2 \times 2$ ), there was virtually no change, with  $w_3 \approx 3.0$  meV [28]. (This behavior of course, points to relatively large multi-site contributions in the zero-point energy.) The magnitudes of these zero-point effects seem quite reasonable; it would be interesting to check for small shifts in phase boundaries when deuterium is substituted for hydrogen [29].

### 2.3. Other aspects

Another effect of interest was the role of local substrate relaxations (i.e. the formation of a surface molecule between the adatom and its substrate nearest neighbors, with consequent weakening [and stretching] of bonds between these nickels and their neighbors). In our calculations for hydrogen, this as negligible, on the order of 0.01 Å or less. To gauge the contribution of this sort of distortion, we froze the clean surface and then added ( $2 \times 1$ ) and  $p(2 \times 2)$  overlayers. Compared to the unfrozen case, the decrease in binding energy in either case was a scant  $\frac{1}{2}$  meV per adatom. Next, forcing a distortion 0.15 Å outward of a triad of surface nickels (as occurs for oxygen adsorption [30]) costs 172 meV. With all Ni's forced outward by 0.15 Å, as would occur for  $(\sqrt{3} \times \sqrt{3})R30^\circ$ , the shortest-range interaction between two such triads is at  $w_5$  (i.e. the centers of the triads, where H would adsorb, are fifth neighbors); even for these strongly perturbed triads, we compute in two cases only a 1 meV repulsion (in comparison with negligible interactions between pairs of H atoms at this separation, with a normal relaxed substrate).

Since EAM and effective medium theory (EMT) make similar approximations, one would expect similar results for lateral interactions. The only EMT study of such energies focused on vibrational shifts for dense H overlayers on Ni(100) and Pd(100) [11]. Consistent with EELS experiments, Nordlander and Holmström [11] found an increase in the frequency normal to the surface. The weakly attractive nature of our zero-point-energy interaction need not imply a disagreement, since we have not projected out the frequencies of individual modes and since decreases in parallel frequencies or substrate modes could outweigh increases in the perpendicular frequency. Both EMT and EAM predict that the coverage dependence of the distance between the H atom and the surface is rather negligible for coverages well below a monolayer, although the direction of change does seem to differ, with EAM predicting outward motion [31]. EMT does take some steps to account for the non-uniformity of the "effective medium" within the H sphere. In EAM the formalism has

been set down [32] to include corrections due to the gradient in the charge density. In a study of the reconstruction of Au(110) [33], these corrections often increased modestly the magnitude of lateral interactions. Moreover, the approximation of linear superposition of spherical charges seems reasonably reliable for Ni surfaces [34].

Well after the completion of these calculations, Truong, Truhlar, and Garrett [16] (TTG) proposed an extension of EAM, called EDIM (embedded diatomics-in-molecules), which leads to magnitudes of interaction energies for H/Ni(111) more in line with our expectations. Specifically, their calculations lead to the values +43.9, +22.6 and +3.5 meV for  $w_2$ ,  $w_3$ , and  $w_4$ , respectively [35]. Since the study focuses on computing potential energy functions for the dissociation of hydrogen molecules, it is not clear which modifications of traditional EAM are most important in producing the larger values of the  $w_n$ 's. However, it seems that the H's are sufficiently separated that the use of valence bond methods for their interaction is not a major source of the change. There are several changes in the form of the EAM functions, but since our results are semi-quantitatively similar for three different sets, it seems likely that the more significant modification is the allowance for the fraction of electrons which are free-electron-like to differ at the surface from in the bulk: in calculating charge densities EAM uses the bulk value of 2 s-electrons for Ni [17], while TTG decrease it to 1.85 for surface Ni's in a compromise effort to fit bond lengths and vibrational frequencies. Remarkably, a self-consistent local-spin-density-functional calculation for Ni(100) [36] found similarly, in a layer-by-layer decomposition of electronic valence charge, that the number of p-electrons at the surface is reduced by 0.14 compared to the lower layers, while all other components are nearly unchanged. This matter invites further study. For example, later work suggests that by adjusting the parameters of the H-Ni and H-H triplet interactions, one can obtain good results for dissociation properties without treating the surface non-d population as a free parameter [37]. In any case, the TTG's lateral interactions are similar in ratio to Roelofs's [3], so that we expect the phase diagram to be at least qualitatively

reasonable, and by scaling the lowest energy excitation [38], we roughly estimate the transition temperature of the  $(2 \times 2)$ -2H at saturation coverage ( $\frac{1}{2}$  ML) to be slightly over 100 K, compared with the experimental value of  $\sim 280$  K.

To summarize our results for H/Ni(111), we find with EAM reasonable signs for the lateral interactions and no unreasonable attractions, but the particular ratio favors a  $(2 \times 1)$  ordering rather than a graphitic  $(2 \times 2)$ . Of greater concern is the small size of the repulsions, over an order of magnitude smaller than required if our lattice gas picture is correct. TTG's EDIM treatment appears to remedy both problems; how the improvement occurs merits further investigation.

### 3. H/Pd(100)

Finally, we briefly considered the adsorption of H on Pd(100), a system that has received much attention [39–42]. Again, we used a nine-layer slab for the substrate. Like set 3 for Ni, the available EAM functions [8] were determined solely on the basis of fits to bulk properties, and so might be less accurate than an analogue of set 1. We found the H sits slightly *below* the surface plane, rather than 0.2 Å above it [41], in the center site. (The clean surface is relaxed inward by 0.11 Å. The H bonds approximately 0.014 Å inside this position, but the four top-layer neighbors move outward, by 0.05 Å for a single H and by 0.20 Å for a monolayer.) Adsorption of an H in a center site is favored by 2.10 eV over an atop site; for compari-

son, calculations that are more sophisticated but require complete  $(1 \times 1)$  overlayers find that the center (above-surface) site is favored over the atop site by 1.06 eV [41]. In earlier work on H/Pd(111) [13], the single-H zero-point energy at subsurface sites differed by 10–20% (for some sites higher, for others lower in value) from that at surface sites. It was furthermore not clear how coverage-dependent effects at these subsurface sites could be translated to surface sites which the H's occupy in reality. In any case, we computed only the classical contribution.

Our results for lateral interactions are tabulated in table 2. We found interaction energies of 87, 53.6, and  $-8.7$  meV for the first, second, and third neighbor configurations, i.e.  $w_1$ ,  $w_2$ , and  $w_3$ , respectively. (See fig. 2a.) Again [13], the two interactions having common substrate atoms are repulsive and roughly proportional to the number of these mutual nearest Pd neighbors (viz., a ratio of 2:1). The ratio contribution  $w_{RT}$  from the smallest right triangle (having two  $w_1$  legs and an  $w_2$  hypotenuse) was  $-25.5$  meV. These magnitudes are sensible (and rather insensitive to vertical location). It is also noteworthy that EAM does produce an *attractive* interaction for the more-distant third neighbor interaction. From analysis of  $(1 \times 1)$ ,  $(2 \times 1)$ ,  $c(2 \times 2)$ , and  $p(2 \times 2)$  overlayers, we deduce 94.1, 54.2,  $-9.0$ , and  $-24.6$  meV for  $w_1$ ,  $w_2$ ,  $w_3$ , and  $w_{RT}$ , respectively, in excellent agreement with the values from isolated configurations. Since  $w_1 < 2w_2$ , the  $(2 \times 1)$  (cf. fig. 2a) is favored over the experimentally observed [39]  $c(2 \times 2)$  (cf. fig. 2b), by 14 meV per H; it was thus rather irrelevant to investigate the details of the

Table 2  
Summary of lateral interactions for H/Pd(100)

No. of shared Pd neighbors:	$w_1$	$w_2$	$w_3$	$w_{RT}$
EAM, classical				
isolated pairs	87	54	$-9$	$-25.5$
ordered overlayers	94	54	$-9$	$-24.5$
Muscat [4]	0	$-70$		
Binder & Landau [40] (units of $w_1$ )	1	$-0.7 \pm 0.1$	$\sim 0$	$> 2$ or $< -3$

Energies are in meV. Configurations for each  $w_n$  are depicted in fig. 2a.

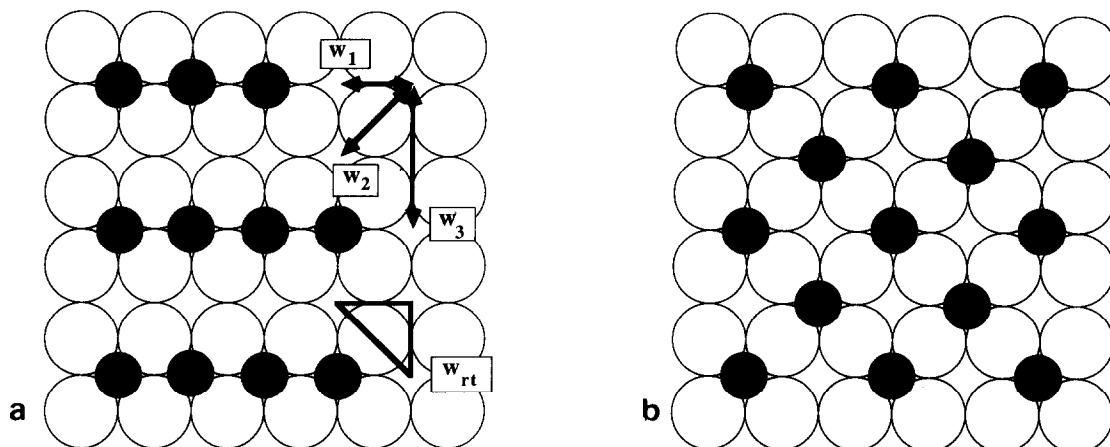


Fig. 2. (a) Schematic of H/Pd(100) illustrating the 4-fold center adsorption site and the separations associated with the lateral interactions  $w_n$ . The three interactions decrease monotonically in magnitude with increasing separation, with  $w_1$  and  $w_2$  repulsive and  $w_3$  attractive. The attractive trio interaction  $w_{RT}$  does not enter the ground state energy of either pattern. In our calculation the stable adsorption site is slightly below the plane of the top Pd layer rather than slightly above it, as observed experimentally [39] and in more sophisticated calculations [41]. EAM predicts the depicted  $(2 \times 1)$ , with lateral energy per H of  $w_1 + 2w_3$ , to be the stable pattern. (b) The  $c(2 \times 2)$  overlayer, with lateral energy per H of  $2w_2 + 2w_3$ , is observed experimentally [39].

phase diagram without modifying the EAM interactions by hand [43].

In comparison, as listed in table 2, Muscat [4] found vanishing  $w_1$  and an attractive  $w_2$  of the same order of magnitude as our repulsion. While these numbers produce a  $c(2 \times 2)$ , they also lead to very broad coexistence regions of  $c(2 \times 2)$  and  $(1 \times 1)$  [3], for which there is no experimental evidence [39]. A general Monte Carlo study by Binder and Landau [40] also proposes such coexistence regions, but implicitly invokes an unphysically strong trio interaction  $w_{RT}$  [44].

#### 4. Conclusions

Given the ease of application of EAM, it is a natural starting point for calculating small energies (and displacements) on metal surfaces. The EAM is intended to indicate trends [45] and to give estimates for relatively complicated systems rather than to produce definitive numbers. The results of our calculations are consistent with this viewpoint. EAM interaction energies for H on Ni are significantly weaker than for H on Pd. Muscat's interactions [4,5a] have similar magnitudes to ours

in both cases, but with signs less consistent with experiment. EAM energies seem "best" (i.e. most consistent with numbers producing the experimental phase diagram) when the H is subsurface, as for H/Pd(111) [13] (and here, slightly and incorrectly, H/Pd(100)). Moreover, the "better" classical energies for H/Ni found by TTG using EDIM [16] suggest that with further refinement, at the expense of more adjustable parameters, one will be able to compute lateral interactions in closer agreement with experiment. We hope this report will motivate careful assessment of the role of each of the modifications made by TTG. Finally, we note suggestions of significant non-lattice-gas aspects in H/Ni(111) (correlated motion of H's out of lattice sites), particularly at low coverages and high temperatures [46].

It would be interesting to see how well EAM does with other adsorbates. Given the tendency of any theory based on the local density approximation to overestimate oxygen bonding (by  $\sim 2$  eV) [47], we do not expect better results for oxygen adsorption than for hydrogen using EAM. On the other hand, EAM has successfully treated alloying at surfaces and phase transitions of adsorbates for one noble metal on another [48]; this may be the

best arena in which to expect the calculated lateral interactions to lead, with minimal tuning, to a phase diagram consistent with experiment.

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