First-principles calculations of adatom binding and interaction on Rh(001)

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The self-consistent scattering-theory approach to adsorption energetics is applied to light atoms, H and S, on a transition-metal surface, Rh(001). A single H adatom is predicted to bind in a four-fold hollow at a height of 1.23 bohr above the outer Rh layer, with a symmetric stretch frequency of 98 meV in the harmonic approximation. A single S atom binds in a fourfold hollow at a height of 2.77 bohr above the surface, indicative of covalent adsorption. Two H atoms fixed at their isolated-adatom equilibrium positions on Rh(001), but in neighboring fourfold hollows, are well screened from each other and hardly interact at all. Under the same conditions, a H and a S adatom are subject to a repulsion of 0.17 eV.

I. INTRODUCTION

Solving classical equations of motion to trace the time development of a prepared atomic configuration is now almost routine, but the results are only meaningful if based on a reasonable interatomic force law.[1] To date, however, little first-principles theoretical input has been available to constrain one's imagination regarding interatomic forces near surfaces. This has limited the possibility of accurately simulating fundamental surface phenomena such as scattering, sticking, dissociation, and diffusion. The work reported here is aimed at improving this situation, showing that the calculation of energy hypersurfaces for light atoms adsorbed on single-crystal transition-metal substrates is possible with modern computational resources. The method used, the self-consistent, matrix Green's-function scattering theory of defect electronic structure,[2,3] has been tested extensively in the context of adsorption on Al(001),[4,5] leading most recently to the prediction and experimental observation of a novel mode of single-atom self-diffusion on fcc(001) metal surfaces.[6] Here the same method, with necessary improvements in numerical accuracy,[7] is applied to H and S adsorption on Rh(001).

The calculations yield reasonable bonding geometries for H and S adatoms, predicting that they reside 1.23 and 2.77 bohr, respectively, above the outer Rh layer of a seven-layer slab, in fourfold hollows. The optimal height of the H atom above the surface corresponds to a location where the electron density of the clean surface is 0.0135 electrons/bohr³. This is expected because of the dominance of the H interaction with the electron gas.[8] The height of the S above the surface corresponds to a S radius of 1.99 bohr, very close to the S covalent radius of 1.97 bohr. The calculated adsorption energy for H is 2.57 eV (neglecting zero-point motion[9]) which agrees well with Richter and Ho's measurement of 2.74 eV.[10] There is no measurement of the heat of desorption for S or S_2 from Rh(001). Comparison of thermal desorption data from Rh(111) and O_2 desorption from Rh(001) suggests an estimate of 4 to 5 eV.[11] A value of either 4.91 or 6.59 eV is calculated for S/Rh(001) depending on whether one

references to an experimental or calculated value of the energy of an isolated S. In agreement with Brand *et al.*'s laser-induced-desorption experiments, showing that S blocks H diffusion on Ru(0001),[12] the interaction between S and H atoms in neighboring hollows on Rh(001) is found to be repulsive. Moreover, in agreement with Richter and Ho's desorption study,[10] H atoms in neighboring hollows neither attract nor repel one another to the accuracy of the calculation. This result follows because the H's are deeply embedded in the Rh surface, and because H atoms perturb the Rh electronic structure weakly. The consequence is that the effect of an H atom is screened out in less than a single atomic spacing. On the other hand, an S atom sits higher above the Rh(001) surface, where screening is less effective. Its perturbation of the surface charge density therefore extends into neighboring hollows so that it can repel a neighboring, adsorbed H.

In the following sections of this article, I briefly review the scattering-theory method (Sec. II), discuss the choice of a localized orbital basis that permits efficient, accurate calculations for a Rh substrate (Sec. III), describe the numerical results obtained for H and S adsorption (Sec. IV), and for H-H and H-S dimers (Sec. V), and briefly discuss prospects for future calculations of energy hypersurfaces for surface chemistry (Sec. VI).

II. SCATTERING-THEORY CALCULATIONS

The results reported here were generated via use of the matrix Green's-function scattering-theory method, which is described in detail in several recent publications.[2-5] Briefly, the method is designed to take advantage of the rapid screening, by metal electrons, of the potential associated with a defect. Because of screening, the wave functions appropriate to a defect or adsorption complex on a metal surface represent Bloch waves that are incident from the region of space where the defect potential vanishes, and that scatter off the defect into outgoing Bloch waves. Scattering wave functions are determined numerically by solving $N \times N$ sets of linear equations, where N is the number of basis orbitals that overlap the

region of space where the defect potential is unscreened. This is the major advantage of the scattering-theory approach. It permits one to determine the electronic structure of an isolated adsorption complex on an otherwise perfect, *infinitely extended* metal crystal surface, by solving a finite matrix problem.

The scattering method is defined within the context of a local-density-functional description of surface electronic structure.[13] The results presented here correspond to the use of the exchange-correlation potential derived by Perdew and Zunger[14] from Ceperley and Alder's[15] electron gas simulations. Nuclear and core-electron potentials are treated via the use of the norm-conserving pseudopotentials of Bachelet et al.[16] The scattering problem corresponds to the solution of the Euler-Lagrange equation for the minimization of the local-density-functional (LDF) theory total energy. This requires solving a self-consistency problem. A scattering potential is guessed, and the corresponding Dyson equation is solved to provide an output electron density in the adsorbate neighborhood. From it, LDF theory permits calculation of an improved scattering potential matrix. The iteration-relaxation scheme of Johnson is used to find an adequately self-consistent electron charge density.[17] Outputs including total valence electron energies and forces on nuclei can then be computed.

III. CHOICE OF BASIS SETS

Before one can hope to compute an adsorption energy, one must define an orbital basis within which the electronic structure of the clean substrate is accurately described. Otherwise some of what appears to be heat of adsorption will be energy gained by the clean substrate when the additional orbitals associated with the adsorbate allow relaxation of substrate electrons into a desirable configuration that was not previously available. I monitor the adequacy of the linear combination of atomic orbitals (LCAO) basis for the seven-layer Rh(001) film, that represents the substrate in the present work, by comparing the LCAO energies of all occupied one-electron levels to corresponding results of a well-converged linear-

ized augmented-plane-wave (LAPW) calculation.[18] I also compare the force on the film's outer layer to the LAPW result. What I find is remarkable, and greatly simplifies the adsorption calculations: a basis comprised of only ten orbitals per Rh atom, plus eight floating orbitals per surface unit cell, yields energy levels that agree to better than 75 meV with the LAPW results at all ten special k points used to perform surface-Brillouin-zone summations. This error level is about as good as one can expect given the inherent inaccuracy of the Bachelet et al. pseudopotential for Rh.[16,19] At the same time, the outer-layer separation of the LCAO film that zeros the force on the outer-layer nuclei is 3.44 bohr (corresponding to a contraction of 3.1%), which is in adequate, if not perfect agreement with the LAPW result, 3.37 bohr. Agreement of the LCAO and LAPW results for the clean Rh(001) film gives confidence that LCAO adsorption energies are meaningful, even though they stem from computations that are not appreciably more costly than they would be if the substrate were Al.

The strategy for choosing basis orbitals is in fact just the same as I used for Al(001).[20] In order to exploit the knowledge that the wave functions near the Rh cores are unaffected by bonding, valence orbitals are selected by fitting linear combinations of Gaussians to accurate pseudo-wave-functions appropriate to the isolated Rh atom. The fits are accurate to distances of roughly 3.5 bohr from the nucleus. At larger distances, the basis functions fall to zero much more rapidly than the isolated atom pseudo-wave-functions do. This prevents numerical problems associated with linear dependence. In order to allow the Rh's $5s$ functions to expand or contract, a second s orbital is centered at each Rh nucleus. Its radial dependence is that of the two longest ranged Gaussians used to describe the valence s function. Inclusion of a second radial d function is found to be unnecessary to achieve good agreement with LAPW results for a clean seven-layer Rh(001) film.

Floating orbitals are included in the basis to allow for electron spillout into the vacuum, and for the Smoluchowski smoothing[21] of electron density corrugation. Effectively, these orbitals restore the variational freedom

TABLE I. Attenuation constants α (in bohr^{-2}) and coefficients c_α for contractions of Gaussians used to represent the electronic structure of the Rh(001) surface. The values given are for radial functions $R_l(r) = r^l \sum_\alpha c_\alpha \exp(-\alpha r^2)$ normalized to $4\pi/(2l+1)$, where l is the orbital angular momentum.

$l=0$			$l=1$		$l=2$	
α	c_α	c_α	α	c_α	α	c_α
0.14	1.246 669 8	1.168 375 7	0.150 000 00	0.449 043 65	0.260 000 00	0.107 509 07
0.22	−0.959 306 63	−0.899 059 73	0.230 591 44	−0.335 416 09	0.847 100 00	0.989 383 13
0.80	−0.760 334 52		1.332 964 9	0.050 661 58	2.256 000 00	3.107 163 1
1.10	0.533 325 80				6.033 000 00	−1.377 789 8

Atop site orbital ($h=3.1$ bohr) $l=1$		Hollow site orbital ($h=4.1$ bohr) $l=0$	
α	c_α	α	c_α
0.19	0.365 953 91	0.19	0.727 076 70

TABLE II. Attenuation constants α (in bohr^{-2}) and coefficients c_α for contractions of Gaussians used to represent the orbitals of H and S adatoms. The values given are for radial functions $R_l(r)=r^l\sum_\alpha c_\alpha \exp(-\alpha r^2)$ normalized to $4\pi/(2l+1)$, where l is the orbital angular momentum.

$l=0$			$l=1$	
α	c_α	c_α	α	c_α
0.17	0.529 194 67	0.626 242 22	1.10	3.286 436 5
0.94	0.656 261 09	−2.543 143 9		
5.00	0.428 186 25	−1.659 308 0		

S-atom orbitals

$l=0$			$l=1$			$l=2$	
α	c_α	c_α	α	c_α	c_α	α	c_α
0.222	0.723 620 43	−1.169 659 3	0.178	0.222 194 78	0.391 643 10	0.180	0.107 509 07
0.850	1.261 773 2	6.959 217 4	0.590	0.670 439 24	−1.953 506 1		
1.550	−2.129 715 4	−5.795 953 2	2.400	−0.175 817 85	0.512 292 88		
3.800	0.416 885 42	1.134 540 5					

that is removed by truncating the Rh valence wave functions relative to those of the isolated atom. Floating s functions, located in fourfold hollows, allow for the Smoluchowski effect. p functions, located directly atop outer-layer Rh atoms, allow for the spillout. The Gaussian attenuation constants and coefficients of all the basis functions used for the clean surface, as well as the locations of their centers, are given in Table I.

Basis sets for H and S adatoms were chosen similarly to that for Rh, with some additional flexibility. For H, I included a $1s$ valence function, fitted to the $1s$ pseudofunction of an isolated H atom. I added a second s function, as well as p_x, p_y, and p_z functions to allow both for changes in the size of the H due to charge transfer and for polarization. For S, as described in a previous publication,[5] I used, in addition to the valence s and p functions, an s-, a p-, and a d-like radial orbital, thus 13 functions in all. The specifics of the H and S basis functions are reported in Table II.

IV. NUMERICAL RESULTS FOR ISOLATED H AND S ADSORPTION

Valence electron energy calculations were performed for H and S atoms individually in fourfold hollow binding sites, for a pair of H adatoms and for an H-S dimer in neighboring hollows. Calculations were also performed for a single H atom in a twofold bridge configuration. In all these cases, for simplicity, the underlying Rh nuclei were fixed at their clean surface positions.[22] In the calculations involving fourfold hollow site bonding, the orbitals assumed to overlap the H- and S-induced surface perturbations were those of the adatoms' first two shells of Rh neighbors (comprising eight atoms) in the outer substrate layer, of the first three shells (nine atoms) in the second layer, and of the first shell (four atoms) in the third layer. In addition, the floating orbitals above the first and second layer Rh's just mentioned were also allowed to participate in determining the self-consistent adsorption-induced charge density. As a result the S-adsorption calculation involved solving 308×308 matrix

Dyson's equations, while the matrix sizes for H, H-H dimer, and H-S dimer adsorption were 300×300, 410×410, and 418×418, respectively. For the bridging H calculation, the same set of orbitals was used as in the H-H dimer case. For fourfold hollow adsorption of a single H on the Rh(001) surface, the induced charge density was neutral to roughly 7×10^{-4} electron. This indicates that screening of the H-related charge is excellent, and correlates with the general observation that the lower an adatom sits on a surface, the more rapidly its surface perturbation is screened. For H in the bridge configuration and for the adsorbed S, charge neutrality was obeyed, respectively, to levels of 1×10^{-3}, and 4×10^{-3} electron. Again this indicates good screening, and gives confidence that the size of the cluster used in solving Dyson's equation is adequate.

Table III provides calculated values of the force on isolated H and S adatoms as a function of their heights above the surface. Evidently, the H binds at a height very close to 1.23 bohr above the outer layer of Rh nuclei, while the S prefers to sit at a height of 2.77 bohr. Putting a parabola through the three values calculated for force versus height of the H adatom yields a force constant of 0.048 Ry/bohr^2. Neglecting the small error associated with the fact that the Rh mass is not infinite, and also neglecting anharmonicity, this force constant corresponds to a prediction of 98 meV for the H symmetric stretch vibration frequency. At the optimal geometry, the H is bound to the Rh by 2.57 eV,[23] in

TABLE III. Calculated force in (mRy/bohr) for H and S vs height (in bohr) relative to the outermost plane of Rh nuclei on the (001) surface.

In fourfold site		In twofold site		In fourfold site	
z	F_z	z	F_z	z	F_z
1.10	6.41	1.98	19.8	2.615	41.7
1.23	0.46	2.23	−13.8	2.765	0.0
1.36	−5.99			2.915	−37.3

reasonable agreement with the measured value of 2.74 eV.[10]

Despite several differences in methodology, the present results are rather close to those which were found in an earlier linearized augmented-plane-wave calculation for a 1×1 H monolayer on Rh(001).[24] This agreement suggests that the interaction of neighboring H adatoms is weak, an idea that is confirmed below via results for a pair of neighboring H adatoms, as well as by experimental measurements of desorption energy versus H coverage.[10] The most important differences between the LAPW and the present calculations, apart from the number of adsorbed atoms are (1) in the LAPW calculation, the lattice parameter was set to its experimental value, 5.083 bohr, rather than the LDF optimal value used here, 5.015 bohr; (2) the Wigner interpolation formula,[25] rather than the Ceperley-Alder potential,[14,15] was used to represent the effects of exchange and correlation; and (3) the Rh substrate was modeled as a three-layer film in the LAPW calculation rather than the seven-layer film used here. Nevertheless, in the LAPW calculation, the optimal height of the H monolayer was 1.1 bohr, the symmetric stretch frequency in the harmonic approximation was calculated to be 100.2 meV, and the H adsorption energy equaled 2.6 eV, all in quite reasonable agreement with the present scattering-theory-based results for a single adsorbed H.

It is, of course, not immediately obvious that an adsorbed H will prefer to reside in a fourfold hollow on Rh(001). In the case of W(001), H adatoms reside at bridge sites. This is presumably a consequence of the small size of H. On an ideal W(001) surface, a H in a fourfold hollow is at least 4.22 bohr from the nearest W atoms. At the same time the W atom radius is only 2.59 bohr. Thus the H bonds weakly to its nearest neighbors. In a bridge configuration, on the other hand, the minimum distance to a W neighbor is 2.99 bohr. So considerably stronger H—W bonds can form, and the bridge site is the preferred one, even though it provides nominally lower coordination for the adsorbed H's. For Rh(001), the minimum distance from a fourfold bonded adatom to a Rh is 3.59 bohr, while the Rh radius is 2.54 bohr. This is much more favorable for an adsorbed H than in the case of W. [The reason for the difference is that the (001) face of a bcc crystal is an open one, while the (001) face of fcc Rh is rather tightly packed.] At a bridge on Rh(001) an adatom can in principle come as close as 2.54 bohr to its neighboring Rh's. But the issue of whether four weaker bonds in a hollow site are preferred to two stronger ones at a bridge is not so clear, and needs to be settled by detailed calculations and experimental observation. In the earlier LAPW work, only one bridge geometry was investigated, for which the height of the H's above the surface layer was chosen to correspond to bond geometries known from organometallic compounds.[24] Thus the H monolayer was placed 2.25 bohr above the outer Rh layer. The adsorption energy per adsorbed H in this configuration was found to be less favorable by 0.17 eV than if the H's were at their optimal height in fourfold hollows. This LAPW result is in good agreement with the present calculation for a single adsorbed H. Linear

interpolation of the results given in Table III shows that the optimal height of a single H above a bridge on Rh(001) is 2.13 bohr. Moreover, at this height the adsorbed H is bound to the surface less strongly by 0.16 eV than at the optimal fourfold site. (All these adsorption
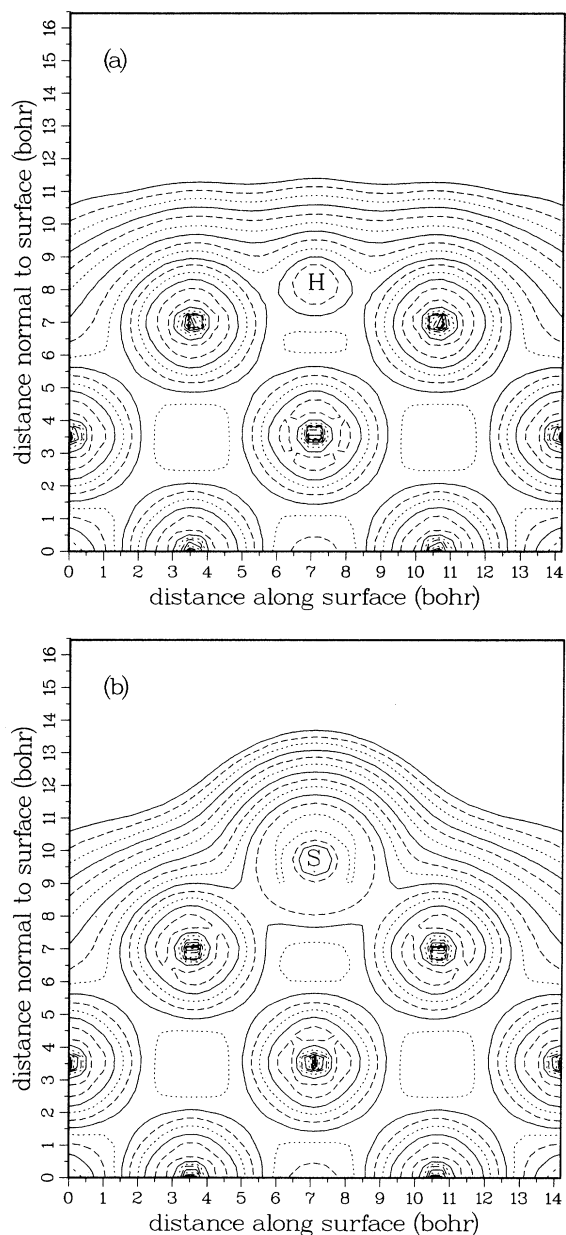

FIG. 1. Contours of constant charge density for (a) a hydrogen adatom, and (b) a sulfur adatom, each in a fourfold hollow on Rh(001). The heights of the adatoms above the outermost Rh layer are 1.23 and 2.77 bohr, respectively, at which each adatom is subject to a force close to zero (cf. Table III). In each case the plane of the plot is perpendicular to the plane of the surface, and passes through the adatom nucleus and two of its nearest-neighbor metal atom nuclei. The vacuum is at the top of each plot. The uppermost contour corresponds to a charge density of 0.001 electron/bohr³. Neighboring contours correspond to a charge-density ratio of 1.58.

energies neglect corrections for zero-point oscillation.[9])
Thus it is reasonable to expect H to bind in fourfold hol-
lows at all coverages up to a monolayer on Rh(001).

Earlier LAPW calculations of the electronic structure
of S overlayers on Rh(001) (Ref. 26) did not include a pre-
diction of the optimal geometric structure, but rather
used the result of a low-energy electron diffraction
(LEED) analysis for the saturation $\frac{1}{4}$ monolayer struc-
ture, $p(2 \times 2)$S-Rh(001),[27] corresponding to S adsorbing
in fourfold hollows with a S—Rh bond length equal to
4.35 bohr. The bond length predicted by the scattering
calculations, for a single adsorbed S, is 4.50 bohr, in fair
agreement with the LEED result. The 4.50-bohr bond
length corresponds to a S radius of 1.99 bohr. This is
very close to the S covalent radius of 1.97 bohr, and sug-
gests that it is appropriate to think of the S—Rh bonding
as covalent rather than ionic. Measurements show that
the work function change induced by a $p(2 \times 2)$ $\frac{1}{4}$ mono-
layer of S on Rh(001) is essentially zero.[28] This is con-
sistent with the idea that the S—Rh bonding is not ionic.

The binding energy of a single S on Rh(001) is calculat-
ed by subtracting the energy of the S/Rh(001) adsorption
system from that of the clean Rh(001) film plus that of an
isolated S atom. If one uses the result of a spin-polarized,
pseudopotential, LDF calculation for the isolated S
atom's energy, one then obtains a S/Rh(001) heat of ad-
sorption equal to 6.59 eV. In reference to the LDF ener-
gy of the isolated S atom, the assumption is that errors
cancel between LDF calculations for S near to and far
from the Rh surface. In fact, there is no evidence that
such a cancellation occurs, and one is free to consider
whether using the experimental energy required to strip
the valence electrons from an isolated S (Ref. 29) provides
a better reference for the evaluation of the valence elec-
tron energy. Since the experimental valence electron en-
ergy of S is 1.68 eV greater than the LDF, pseudopoten-
tial value, using the experimental energy as a reference
implies that the S/Rh(001) heat of adsorption is only 4.91
eV. Even this value seems on the high side compared to
the rather scanty measurements available in the litera-
ture,[11] but is definitely more reasonable than 6.59 eV.

In Fig. 1, charge-density contour plots are provided for
H and S adsorption on Rh(001). The H atom is seen to
lie rather close to the outer Rh layer, and to perturb the
charge density quite weakly and locally. Since its effects
are so well screened, it is reasonable to expect that neigh-
boring ground-state H's will not interact strongly. This
expectation is confirmed in results for a pair of H's, as de-
scribed in the following section. The larger S adatom,
represented in Fig. 1(b), lies higher above the surface,
where screening is less effective, and its effects therefore
extend farther laterally. The charge contours around the
S are noticeably nonspherical. This reflects the presence
of nonbonding p electrons pointing out into the vacuum.
If the S resided farther from the outer Rh layer, the
bonding would be more ionic, and the charge contours
about the S would be more symmetric.

V. RESULTS FOR H-H AND H-S ADSORBED DIMERS

A major objective of scattering-theory calculations is
to provide information concerning the energy hypersur-

TABLE IV. Calculated force (in Ry/bohr) for the geometries
given (position vectors in bohr) of a H-S dimer adsorbed on
Rh(001) and for a H-H dimer on the same surface.
(0.000,0.000,0.000) and (5.015,0.000,0.000) are fourfold hollows
in the outermost plane of Rh nuclei.

Adatom	Adatom position	Force on nucleus
H	(0.000,0.000,1.230)	(−0.013,0.00,−0.006)
S	(5.015,0.000,2.765)	(0.016,0.00,0.003)
H	(0.000,0.000,1.230)	(−0.002,0.00,−0.001)
H	(5.015,0.000,1.230)	(0.002,0.00,−0.001)

faces that determine how surface chemical phenomena
proceed. In this section results are presented for pairs of
light atoms adsorbed on a transition-metal surface. Fur-
ther calculations, aimed at exploring the corrugation of
the potential seen by an incident H_2 molecule, are under
way.

Laser-induced-desorption experiments by Brand
et al.[12] imply that H atoms on a Ru(001) surface avoid
substantial sized regions surrounding coadsorbed S
atoms. This could account microscopically for the ability
of S to poison chemical reactions in which H combines
with other adsorbed species. One might expect a similar
repulsive H-S interaction to obtain on Rh(001), and to ex-
amine this possibility, LDF calculations were carried out
for H and S atoms adsorbed in neighboring fourfold hol-
lows. The H and S were each fixed at the height above
the surface at which it would be optimally located if the
other atom was not present. Then the adsorption energy
of the pair and the force on each nucleus was determined.
The result is that the H-S interaction is indeed repulsive.
The adsorption energy is reduced by roughly 0.17 eV rel-
ative to widely separated adatoms. The forces on the two
atoms are away from each other, and directed mainly
parallel to the surface (see Table IV). This latter fact sug-
gests that the interaction is primarily direct and not
"through metal." Through metal interactions lead to
substantial forces pushing the adatoms away from the
surface.[30] They are obviously dominant at larger H-S
separations.

The case of the adsorbed H dimer is quite different,
presumably because the H atoms lie so close to the outer-
most Rh layer. When two H atoms are in neighboring
hollows, at the sites where each would be optimally locat-
ed if the other were absent, there is no pair interaction
energy, to within the accuracy of the calculation, and
only very small forces on each nucleus. This result is not
unexpected, given the agreement found for the geometry
and symmetric stretch frequency for a H monolayer, us-
ing the LAPW method,[24] and for a single adsorbed H
atom in the scattering calculations (cf. the results men-
tioned in Sec. I above). It also accords with the desorp-
tion energy measurements of Richter and Ho,[10] who find
that for coverages of H on Rh(001), from 0 to 0.8 mono-
layers, the desorption energy of H does not vary. (Above
0.8 monolayers, residual CO on their surface complicates
their analysis.) Figure 2 indicates the reason for the weak
H-H interaction relative to the substantial H-S repulsion.

Figure 2(a) shows that the charge density associated with an adsorbed S overlaps the neighboring adsorbed H, while the charge densities of two neighboring adsorbed H's hardly seem to overlap at all.

Richter and Ho[10] do observe that the vibration spectrum of H/Rh(001) is H-coverage dependent. For example, the energy of the fundamental symmetric stretch
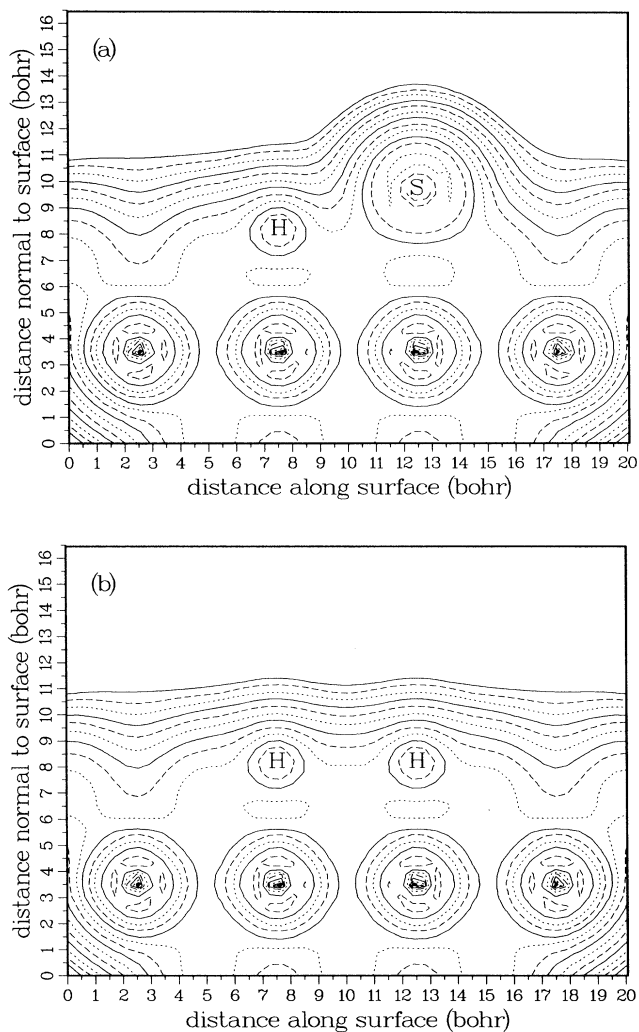

(a)

distance normal to surface (bohr)

distance along surface (bohr)

(b)

distance normal to surface (bohr)

distance along surface (bohr)

FIG. 2. Contours of constant charge density for (a) an adsorbed H-S dimer on Rh(001), and (b) an adsorbed H-H dimer on the same surface. In each case the adatoms are fixed in symmetric fourfold hollow sites at heights above the outermost Rh layer where the force would be zero if the other adatom were absent. In each case the plane of the plot is perpendicular to the plane of the surface, and passes through the adatom nuclei and also through second-layer Rh nuclei. The vacuum is at the top of each plot. The uppermost contour corresponds to a charge density of 0.001 electron/bohr^3. Neighboring contours correspond to a charge-density ratio of 1.58. Since the charge for these plots is calculated by inclusion of only the contributions of the orbitals that overlap the adatom-induced potential, the odd-looking contours in the lower right- and left-hand corners reflect the absence of contributions from orbitals outside this set, rather than physics.

mode increases from 70 to 82 meV as the H coverage increases from 0.32 to 1.0 ML. They attribute this effect to a dynamical interaction of adsorbed H's, which leads to a weaker effective force constant when an adsorbed H has one adsorbed H neighbor or none, and a stronger one when it has three or four neighbors. Explaining this relatively small effect via further calculations for a cluster of adsorbed H's is an interesting challenge.

The close comparison, noted in Sec. I, of calculated symmetric stretch frequencies for a H monolayer using the LAPW method,[24] and for a single adsorbed H using the scattering method, does not prove that LDF theory is unable to account for the coverage dependence of the H/Rh(001) vibration spectrum. The methodological differences in the two calculations, e.g., the use of different exchange-correlation potentials and the fact that one calculation used the rigid core approximation while the other was based on norm-conserving pseudopotentials, may well have been large enough to mask the dependence of the force constants on the number of H neighbors.

VI. DIRECTIONS

The encouragingly reasonable results of these first calculations of the interactions of light atoms on a transition-metal substrate suggest that it would be worthwhile performing many more of them. Even when only two atoms are adsorbed on a crystal surface, the number of configurations necessary to form a useful picture of the energy hypersurface is large. As an example, the fact that the energy difference between H at a bridge and H in a fourfold hollow is only 0.16 eV means that an adsorbed H will explore a good deal of the surface unit cell and, at not particularly elevated temperatures, will often hop from one cell to another. Thus the single geometry for which the H-H interaction has here been calculated represents only a small portion of the configuration space visited by an interacting H-H pair.

This means that one must either commit to spending a great deal of computational effort per problem of interest, or one must seek ways to reduce the calculational cost per adatom geometry. Plane-wave basis, supercell methods offer one possible direction for research.[31] The main difficulty is that numerous atomic species cannot be described in terms of a suitably small number of plane waves. Moreover, when there are many atoms in the supercell, the number of occupied levels is large and the scaling of the plane-wave schemes becomes unfavorable.

There is some hope that the scattering method can be made more efficient. Scheffler et al. have developed a variant of the scheme described in Sec. II in which the kinetic energy does not contribute to the matrix elements of the effective scattering Hamiltonian.[32] As a result, the range of this Hamiltonian is shorter than in the matrix Green's-function method of Williams et al.,[2] and charge densities can be obtained by solving smaller sets of scattering equations. Since the computational effort in-

volved in solving an $N \times N$ set of linear equations scales as N^3, the method of Ref. 32 promises to make the scattering method significantly more efficient. On the other hand, it has not yet been learned whether the savings of the new approach will be obtained at a cost in accuracy of the calculated adsorption energies and forces. If the accuracy of the method does prove adequate, obtaining similar savings in the matrix Green's-function method[2,3] looks straightforward.

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