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Model for the electrocatalysis of hydrogen evolution

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We show how a theory for electrocatalysis developed in our group can be combined with density-functional theory in order to obtain free-energy surfaces for electrochemical reactions. The combined theory is applied to the first step in the hydrogen evolution reaction, which is a proton transfer from an electrolyte solution to a metal electrode. Explicit calculations have been performed for five metals: Pt, Au, Ag, Cu, and Cd. In accord with experimental findings we find a high activation energy for Cd, medium values for the coin metals, and on Pt the transfer occurs with little activation. These results are explained in terms of the position of the *d* band of these metals and their interactions with the hydrogen 1*s* orbital as the latter passes the Fermi level in the presence of the solvent.

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I. INTRODUCTION

During the last decades there has been tremendous progress in theoretical surface science. Due to the great improvement of computer power and the development of efficient algorithms it has become possible to understand surface structures and processes in terms of electronic interactions. Much of this progress has been based on density-functional theory (DFT), which combines computational efficiency with an acceptable accuracy.[1] Consequently, the principles of catalytic activity have been elucidated for a fair number of reactions, and in the famous example of steam reforming DFT calculations have played an important role in the development of an efficient catalyst.[2]

Although electrochemistry has much in common with surface science there has been no comparable progress in our understanding of electrocatalysis. The reasons for this are obvious: all proper electrochemical reactions involve electron transfer, in which the solvent plays a crucial role, as we know from Marcus theory.[3] Therefore, realistic calculations would have to include a fair amount of water molecules at room temperature, which entails ensembles of prohibitive size. Also, electrochemical reactions are governed both by the surface charge of the electrode and by the electrode potential, and so far it has not been possible to include both in a realistic way in model calculations.

In our group we have taken the view that realistic DFT calculations or simulations for electrochemical reactions are impossible at this time, and may not even be desirable, since they may imitate the reaction rather than explain it. A proper understanding should be based on a theory, which, of course, may require the results of extensive calculations as input. As our starting point for such a theory, we have taken a model Hamiltonian for electrochemical bond-breaking reactions proposed by Santos *et al.*,[4,5] which combines ideas of Marcus theory, the Anderson-Newns model,[6,7] and the tight-binding (or Hückel) theory. On the basis of this Hamiltonian two of us (E.S. and W.S.) have proposed a mechanism,[8,9] by which a metal *d* band interacting strongly with the valence level of the reactant may broaden the latter's density of states (DOS) *as it passes the Fermi level*, and thereby enhance the reaction rate. We shall return to this model below. A first application of these ideas[10] explained well the trends in the catalysis of the hydrogen oxidation reaction in terms of the position of the metal *d* band and its coupling to the hydrogen 1*s* orbital, concepts which are familiar from the adsorption of hydrogen from the gas phase.[11] However pleasing these results may be, they suffered from the usual limitations of Anderson-Newns-type models, which may explain trends, but do not give quantitative results because important exchange and correlation terms are missing. Therefore, in this work we suggest a way to incorporate the missing energy terms into our model for electrocatalysis by incorporating the results from DFT calculations. This makes it possible to calculate free-energy surfaces, as a function of the reactant's position and the solvent coordinate, for electrochemical reactions. We apply our theory to the first step in the hydrogen evolution reaction, which is the transfer of a proton from the solution to the electrode surface, and perform model calculations for several metals. Our results do not invalidate our previous work, but allow a more detailed and more quantitative understanding of electrocatalysis. A simplified version of our work, yielding one-dimensional (1D) reaction curves rather than surfaces, has been published before,[12] and a model surface has been presented in a special issue dedicated to J. O'M. Bockris,[13] but this is the first report on the details of our method and its application to several metals.

The rest of this paper is organized as follows: for completeness, we recapitulate the theory of electrochemical electron transfer on which our further developments are based, and show how it can be combined with DFT calculations in order to correct the well-known shortcomings of Anderson-Newns-type models. We then show, how the relevant system parameters can be obtained from DFT, and then apply our theory to the hydrogen evolution on a series of metals. Specifically, we have chosen Cd as an example of bad catalysts, the three coin metals Cu, Ag, and Au as mediocre, and Pt as an excellent catalyst.

II. HYDROGEN-METAL INTERACTION

We focus on the electrochemical adsorption of a proton from the solution onto the surface of a metal electrode

$$H^+ + e^- \rightarrow H. \tag{1}$$

This is the rate-determining step in the hydrogen evolution reaction on all the metals that we consider explicitly below. Since it involves only a simple electron transfer and no bond breaking, we can apply the theory of simple electrochemical electron transfer.[14] The model Hamiltonian consists of terms for the relevant electronic part of the system—the 1*s* orbital on the hydrogen atom and the electronic states on the metal electrode—and terms for the solvent. We denote with the index a the hydrogen 1*s* orbital, by ϵ_a its energy, and by n_a the corresponding number operator; the metal states are labeled k and thus have energies ϵ_k and number operators n_k. As we will detail below, all calculations will be performed at short reactant-metal separations so that only nonmagnetic states play a role. Therefore, spin plays no direct role, and the electronic Hamiltonian is

$$H_{\mathrm{el}} = \epsilon_a n_a + \sum_k \epsilon_k c_k + \sum_k [V_k c_k^+ c_a + V_k^* c_a^+ c_k]. \tag{2}$$

The last term effects electron exchange between the metal and the reactant; c^+ denotes a creation and c an annihilation operator.

The interaction of the reactants with the solvent is of prime importance, and particularly in the case of proton, which has a hydration energy of the order of 11.5 eV. As in the theory of Marcus[3]—which in turn is based on polaron theory—we distinguish between fast and slow solvent modes. The slow modes correspond to the motion of the nuclei, and it is their fluctuations that shift the electronic level of the reactant and induce electron transfer. The fast electronic modes are supposed to follow the slow modes adiabatically, and therefore renormalize the electronic energy. We include the slow modes explicitly in our model Hamiltonian, and return to the fast ones later. The slow solvent modes are modeled as a phonon bath, which interacts linearly with the charge $(1-n_a)$ on the reacting hydrogen. Other models such as a description by a polarization field[3] or through charge-dipole interactions[15] give the same results; the important point is that the Hamiltonian is of second order in the coordinates, and that the coupling to the external charge is linear. The corresponding terms in the Hamiltonian are

$$H_{\mathrm{sol}} = \frac{1}{2}\sum_\nu \hbar\omega_\nu (q_\nu^2 + p_\nu^2) + (1-n_a)\sum_\nu \hbar\omega_\nu g_\nu q_\nu. \tag{3}$$

Here ν labels the phonon modes, q_ν and p_ν are the dimensionless coordinate and momentum operators, and in the last term g_ν is the interaction constant of the charge with the mode ν. The interaction of the solvent with the reactant is characterized by the energy of reorganization $\lambda = \Sigma_\nu \hbar\omega_\nu g_\nu^2/2$.

When all solvent modes are classical, they can be combined into one effective solvent coordinate q.[14] This can be achieved by a coordinate transformation: $x_\nu = q_\nu/g_\nu$; in these transformed coordinates, the minima and saddle points of Eq. (3) are always on the same straight line, and q can be taken to indicate the position on this line. Further, q can be normalized such that it takes on the following meaning: when the configuration of the slow solvent modes is characterized by a certain value q, it would be in equilibrium with a charge of $-q$ on the reactant. In particular, $q=0$ corresponds to the discharged hydrogen atom, and $q=-1$ to the solvated proton. Since this representation by one effective mode implies an average over all but one solvent degrees of freedom, the resulting energies have the meaning of a free energy as in Kramers theory.[16] We emphasize that our theory is not restricted to such a treatment of the solvent, which is on the level of the Marcus theory, but at the moment not much is known about the details of proton hydration at interfaces. In any case, the focus of this paper is on the role of the metal, in particular on their catalytic activities. Since the interaction of water with the metals that we consider is weak, we may use the same simple model for solvation in all these cases.

The total model Hamiltonian is the sum of the two parts $H_{\mathrm{el}}+H_{\mathrm{sol}}$. The Greens function of the electronic part can be calculated exactly as a function of the generalized solvent coordinate q; in particular, the density of states of the hydrogen orbital is

$$\rho_a(\epsilon) = \frac{1}{\pi}\frac{\Delta(\epsilon)}{\{\epsilon - [\epsilon_a + \Lambda(\epsilon) - 2\lambda q]\}^2 + \Delta(\epsilon)^2}. \tag{4}$$

Here, $\Delta(\epsilon)$ and $\Lambda(\epsilon)$ are the chemisorption functions

$$\Delta(\epsilon) = \sum_k |V_k|^2 \pi \delta(\epsilon - \epsilon_k), \quad \Lambda(\epsilon) = \frac{1}{\pi}\mathcal{P}\int \frac{\Delta(\epsilon')}{\epsilon - \epsilon'} d\epsilon'. \tag{5}$$

The total energy of the hydrogen atom and the solvent, as a function of the solvent coordinate q, is then

$$E(q) = \int_{-\infty}^{0} \rho_a(\epsilon)\epsilon d\epsilon + \lambda q^2 + 2\lambda q, \tag{6}$$

where the Fermi level has been taken as the energy zero. The first term is the electronic energy of the hydrogen atom modified by the interaction with the solvent, the other two terms pertain to the solvent and its interaction with the proton. Up to here, there is nothing new in our model. It suffers from the well-known shortcomings of Anderson-Newns-type theories, which neglect exchange and correlation energies between the reactant and the metal electrons. Nevertheless, such theories can be used to predict trends, and for this purpose they have been successfully applied both to hydrogen adsorption in the gas phase[17] and by our group[10,18] to the electrochemical hydrogen oxidation. The distinct feature of our work is that we combine this model with DFT calculations, which we use for two purposes: to correct for the missing electronic energy terms and to obtain the chemisorption functions $\Delta(\epsilon)$ and $\Lambda(\epsilon)$.

The energy term that is missing in Eq. (6) is for the correlation and exchange between the electrons on the metal and on the hydrogen atom. To correct for this, we note that for $q=0$ the solvent has no effect on the electronic energy, and we can use the results of DFT. Because of its high ionization energy the adsorbed hydrogen is neutral on all metals, i.e., the occupation of the hydrogen orbital is unity. As long as this occupation does not change, solvent fluctuations should have no effect on the electronic energy, and the DFT result applies. However, for large solvent fluctuations the occupancy changes, and it finally becomes zero. In the latter case there are no electrons on the hydrogen, its electronic energy vanishes, and there is no correlation or exchange with the metal to correct for. We therefore use the following procedure: we calculate the electronic energy of hydrogen both from DFT and from the first term in Eq. (6) for $q=0$. The difference ΔE is the error of the model for $q=0$. We now assume that for other values of q the error is proportional to the occupancy $\langle n_a\rangle$ of the hydrogen orbital

$$\Delta E(q) = \Delta E(q=0)\langle n_a\rangle. \tag{7}$$

This equation is obviously correct in the limits when $\langle n_a\rangle=1$ and $\langle n_a\rangle=0$. The linear interpolation is natural, and DFT itself is based on interpolations of this kind. In effect, we use Eqs. (4) and (7) to extrapolate the DFT results, which are valid for $q=0$, to other values in the range of $-1\le q\le 0$.

Finally, we have to consider the energy of the proton with its environment. With the terms given above, the energy of the proton would be just $-\lambda$, but this is only the interaction with the slow solvent modes. The parts that are missing are the interactions with the fast solvent modes, the image force on the proton, and the interaction with the electrostatic potential. Fortunately, we do not have to consider them explicitly, since we know that at the equilibrium potential the free energy of the proton must be one half of the free energy E_i of the hydrogen molecule. Therefore we add a term

$$V_f = (1-\langle n_a\rangle)(E_i/2+\lambda-e_0\eta) \tag{8}$$

to the total energy of the system. Again, the interaction has been assumed to be proportional to the charge. The last term accounts for the effect of an overpotential η. The energy of the H_2 molecule is -31.73 eV, and the entropic contribution is -0.41 eV,[11] which gives $E_i=-32.11$ eV. We have used a simple and natural interpolation.

III. INTERACTION PARAMETERS

To obtain the density of states of the hydrogen orbital we require the two chemisorption functions $\Delta(\epsilon)$ and $\Lambda(\epsilon)$, the electronic level ϵ_a, and the reorganization energy λ. We first discuss the first three, which pertain to the electronic properties. All metals considered have a broad *sp* band and a narrower *d* band. Accordingly, we split the interaction up into two parts $\Delta(\epsilon)=\Delta_{\mathrm{d}}(\epsilon)+\Delta_{\mathrm{sp}}(\epsilon)$. The interaction with the *d* band causes catalysis; we assume that it is independent of the electronic energy ϵ, so that

$$\Delta_{\mathrm{d}}(\epsilon) = |V|^2\pi\rho_{\mathrm{d}}(\epsilon), \tag{9}$$

where $\rho_{\mathrm{d}}(\epsilon)$ is the DOS of the metal *d* band and $|V|^2$ is the interaction constant. The *sp* bands are broad on all metals. For the sole purpose of obtaining the interaction constant $|V|^2$ of the *d* band, it suffices to use the wideband approximation for the *sp* band. However, in order to avoid the logarithmic energy divergence associated with this approximation we have followed Newns[7] and used a semielliptic band instead, which follows naturally from a one-dimensional tight-binding model. So we set

$$\Delta_{\mathrm{sp}}(\epsilon) = \Delta_0\left\{1-\left[\frac{(\epsilon-\epsilon_c)}{w_0}\right]^2\right\}^{1/2}\theta(w_0^2-\epsilon^2). \tag{10}$$

In all calculations, we have set the center ϵ_c of the *sp* band at the Fermi level and its half width w_0 to 15 eV. As long as this band is sufficiently wide, the exact values have no effect on the results. Instead of a semielliptic band one can also use a wideband with a constant Δ_{sp} and a bottom well below the Fermi level.

Since $\Lambda(\epsilon)$ is determined from $\Delta(\epsilon)$ through a transform, this leaves three parameters to be determined: $|V|^2$, ϵ_a, and Δ_0, and we need them as a function of the distance between the hydrogen atom and the metal. For this purpose, we have performed DFT calculations for various separations. The technical details are given in the Appendix; here we only discuss those points that are of immediate interest. First, calculations were performed for the bare metals, with relaxation of the upper two layers. Then, a hydrogen atom was added and the equilibrium position determined. For the fcc metals Pt, Au, Ag, and Cu, the optimum position for hydrogen adsorption was always the fcc threefold hollow site; for Cd(0001) it was the threefold hollow site. This finding is in agreement with that of most workers, although on Pt(111) Ishikawa *et al.*,[19] using different functionals, found the bridge site more favorable. In fact, on Pt(111) the adsorption energies on the hollow, bridge, and on-top sites are quite similar, and different pseudopotentials or exchange-correlation functionals may give slightly different results. Once the equilibrium position for the adsorbed hydrogen atom had been found, calculations were performed for a series of atom-metal separation. These calculations were performed both with and without further relaxation of the surface. The two sets of calculations differ only at very short distances on the order of 0.1–0.2 Å from equilibrium, and by less than 0.1 eV; they give identical results for the free energies of activation. We show the surfaces obtained without further relaxation, for the following reason: when we let the metal relax, at short separations the top atoms followed the hydrogen atom a little, because of the elasticity of the metal. However, proton/hydrogen transfer from the solution to the surface, and vice versa, is triggered by a fluctuation of the solvent. At a suitable solvent configuration the proton/hydrogen is rapidly exchanged. Since the time scale at which the light-transferring particle moves is shorter than the time scale of the heavier metal atoms, the transfer should occur without further surface relaxation.

Calculations were performed up to a separation of 3 Å for the surface in steps of 0.1 Å. In accord with the findings of Mizielinki *et al.*[20] spin polarization did not occur for separations smaller than 2.4 Å; for larger separations it was observed in some systems. We shall see later that at such large separations the hydrogen is fully ionized according to our model, so that spin polarization could be ignored, even though it can easily be included.

At each separation, we obtained the energy of adsorption of the hydrogen and the DOS projected onto the hydrogen 1*s* orbital. The latter was then fitted to Eq. (4) with $q=0$, using

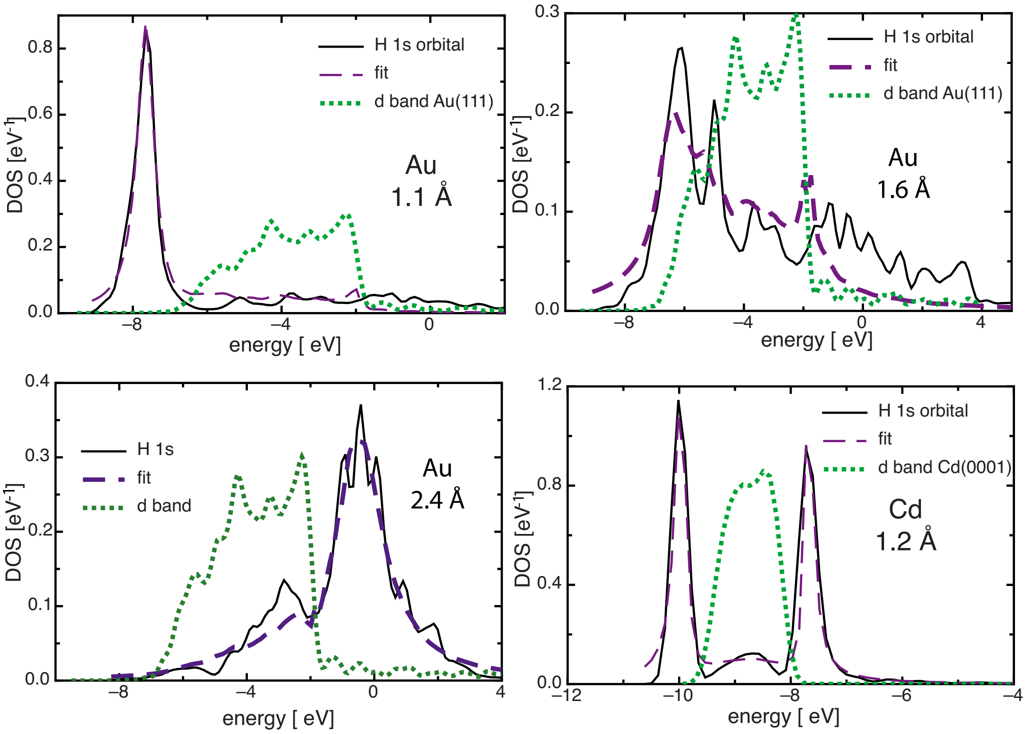

FIG. 1. (Color online) Examples for the DOS of the hydrogen 1*s* orbital as obtained for DFT and from the fitting procedure; the metal *d* bands are also shown. (a)–(c) H on Au(111) at various distances; (d) H on Cd(0001).

$|V|^2$, ϵ_a, and Δ_0 as parameters. Figure 1 shows a few examples for the hydrogen DOS obtained from DFT along with the fitted curves; all DOS have been normalized so that their integral is unity. On Au(111), at short distances the hydrogen 1*s* orbital lies below the metal *d* band: this is true for all metals considered except for Cd. The interaction with the gold *d* band spreads the hydrogen DOS toward higher energies and thus determines the area under the major peak. Fitting poses no problem and is excellent. The situation becomes more difficult at intermediate distances, where the hydrogen orbital lies within the *d* band. Here the fitted curve does not reproduce all of the details, but is still a good representation, and the values obtained for $|V|^2$ and ϵ_a join smoothly the values obtained for neighboring distances. Also, it should be borne in mind that the DOS obtained from DFT are not perfectly defined, and minor features such as the oscillations near the Fermi level may well be artifacts. Increasing the number of *k* points generally reduces the number of such minor oscillations (see Appendix), and for this reason we have used more *k* points than would have been necessary for energy convergence alone. At larger distances, the hydrogen DOS lies above the *d* band of gold, and the fit is very good. Cd(0001) is an interesting case: at short distances the hydrogen level lies right in the *d* band and is split into a bonding and an antibonding part. Since both parts are occupied, no bonding results; the equilibrium distance is longer than at the other metals, and the adsorption energy higher.

The interaction constants $|V|^2$ obtained from this fitting are shown in Fig. 2. As expected, at somewhat larger distances, beyond 1.3 Å, they decrease in the order Pt$>$Au$>$Ag$>$Cu and fall off with the distance. At short distances, the interaction of Cu with hydrogen is somewhat higher than for Ag, but it falls off more rapidly because of its smaller atomic radius. For Cd the interaction is initially quite high, but falls off more rapidly with the distance than for the other metals. Since its *d* band lies so low, this comparatively large interaction has no catalytic effect, as we shall show below. The hydrogen level ϵ_a increases with distance (see Fig. 3), an effect that is well known and mainly caused by the interaction with the *sp* band and the screening of the Coulomb repulsion between the two spin states. The increase is quite similar in all cases investigated, indicating that the behavior of the *sp* bands differs little between these metals.

Another quantity of interest is the energy of adsorption of a hydrogen atom on the metal surface on the hydrogen scale, using hydrogen at standard conditions as energy reference. These were obtained by calculating the energy change as a

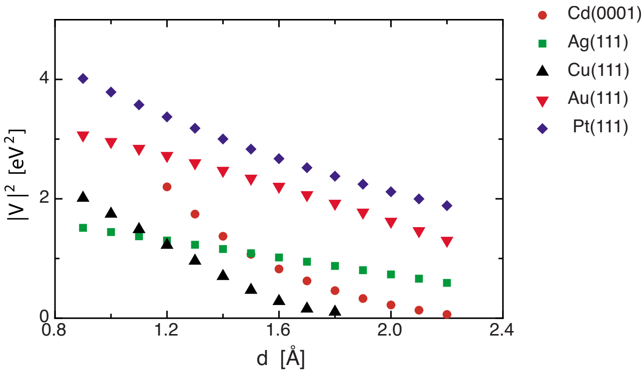

FIG. 2. (Color online) Interaction constants $|V|^2$ in eV^2 as a function of the distances for the metals investigated.

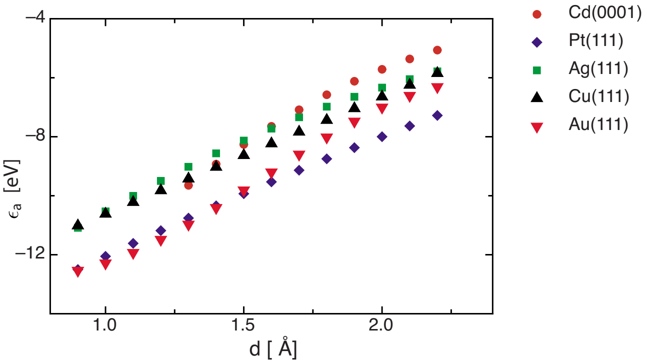

FIG. 3. (Color online) Hydrogen level ϵ_a as a function of the distances for the metals investigated, taking the vacuum as the reference level.

hydrogen molecule approaches the metal surface from a long distance and separates into two adsorbed hydrogen atoms. As suggested by Nørskov *et al.*,[11] an amount of 0.2 eV was added to these values in order to account for the entropy of the hydrogen gas and the zero-point energy of the H_2 molecule. No correction was made for the zero-point energy of the adsorbed atom, which we found to be on the order of 0.04 eV in the vacuum, in agreement with Nørskov *et al.*[11] This small value would be reduced by the presence of the solvent, and also partially cancelled by the entropy of the adsorbate, which for intermediate coverages is negative. In any case, such small contributions, which are practically the same for all metals, are irrelevant since they are smaller than the accuracy of DFT calculations. The resulting values ΔG_{ad} are given in Table I; they are close to those given by Nørskov *et al.*,[11] smaller differences being due to technicalities such as the use of the slightly different functional (PBE in our case, RPBE in Ref. 11).

For the electron transfer the interaction of the proton with the solvent is just as important as that with the metal. In the cases considered the interaction of water itself with the metal is weaker than the interaction between the solvent molecules, so that we may expect that the nature of the metal has little effect on the energy of solvent reorganization λ. Based on an energy of solvation of about 11.5 eV for the proton, we have previously estimated that λ lies in the range of 3 to 4 eV.[10] Fortunately, the exact value is not so important since λ appears also in the proton energy V_f in Eq. (8) and there is a partial cancellation. Another question is the variation in λ in the surface region. Using a constant value has the obvious advantage that we do not need to introduce more parameters. However, from a physical point of view we would expect that λ increases from the surface toward the bulk. In previous publications it has been suggested that right at the surface λ is smaller by about a factor of two,[21,22] and used a simple interpolation between surface and bulk values

$$\lambda(d) = \lambda_\infty \frac{1 + p(d/L)}{2}, \quad p(x) = \begin{cases} 0 & \text{for } x < 0 \\ (3-2x)x^2 & \text{for } 0 \leq x \leq 1 \\ 1 & \text{for } 1 < x, \end{cases} \tag{11}$$

where λ_∞ is the value in the bulk, which falls off by a factor of 2 over a distance of L. The interpolating polynomial has been chosen such that it interpolates over the two limiting values with zero gradient at the end point. In our model calculations, we have used both Eq. (11) and a constant value of λ to explore the consequences.

TABLE I. Free energy ΔG_{ad} of adsorption of a hydrogen atom on the hydrogen scale in eV.

Metal	Cd	Cu	Ag	Au	Pt
ΔG_{ad}	0.91	0.10	0.39	0.41	−0.25

IV. FREE-ENERGY SURFACES FOR HYDROGEN ADSORPTION

Our aim is to explore the *d* band catalysis of the hydrogen evolution on various metals. The pertaining parameters $|V|^2$, ϵ_a, and ΔG_{ad} have been directly obtained from DFT. There are two other parameters that enter: the *sp*-induced width Δ_0, and the energy of reorganization λ. The latter are expected to be about the same for all metals discussed, and will therefore, at least within our model, not affect the relative quality of the catalysts. For the interaction with the *sp* band, our fitting procedure suggests a value of about $\Delta_0 = 0.7$ eV as a good average value. It would be a little smaller at large separations, but there its value is not important since the hydrogen has already lost its electron. Henceforth we shall use $\Delta_0 = 0.7$ eV, which is our best estimate.

When we use a model with a constant energy of reorganization λ, its exact value has only a small effect, as long as it is within a reasonable range, i.e., 3–4 eV according to our estimates. Taking Ag(111) as an example, we obtain activation energies of $E_{\text{act}} = 0.57$ and 0.62 eV for $\lambda = 3$ and 4 eV, respectively. This weak dependence is caused by the partial cancellation discussed above.

Of greater interest is the effect of a variation in the reorganization energy λ in the surface region. Figure 4 shows two free-energy surfaces for adsorption on Ag(111). For the left surface, a constant value of $\lambda = 3$ eV was assumed, on the right we have used a λ that varies according to Eq. (11) with $\lambda_\infty = 3$ eV and a decay distance of $L = 1.5$ Å, an estimate based on molecular-dynamics simulation for proton transfer on platinum performed in our group.[23] Both surfaces show the same main features: a minimum near $q = 0$, $d = 0.9$ Å corresponding to the adsorbed hydrogen atom, and another minimum at $q = -1$ at larger distances from the surface corresponding to the solvated proton; on silver, the adsorption step is uphill, so the free energy of the adsorbed hydrogen is higher than that of the proton. Both minima are separated by a saddle point; the associated energies of activation with respect to the solvated proton in solution are $E_{\text{act}} = 0.57$ and 0.71 eV for the constant and the variable λ, respectively. On the left surface, the minimum for the proton is at shorter separation from the surface, because the solvation is strong everywhere; this minimum is somewhat deeper than on the right surface, because it occurs in a region where the proton still carries a small electronic charge that interacts

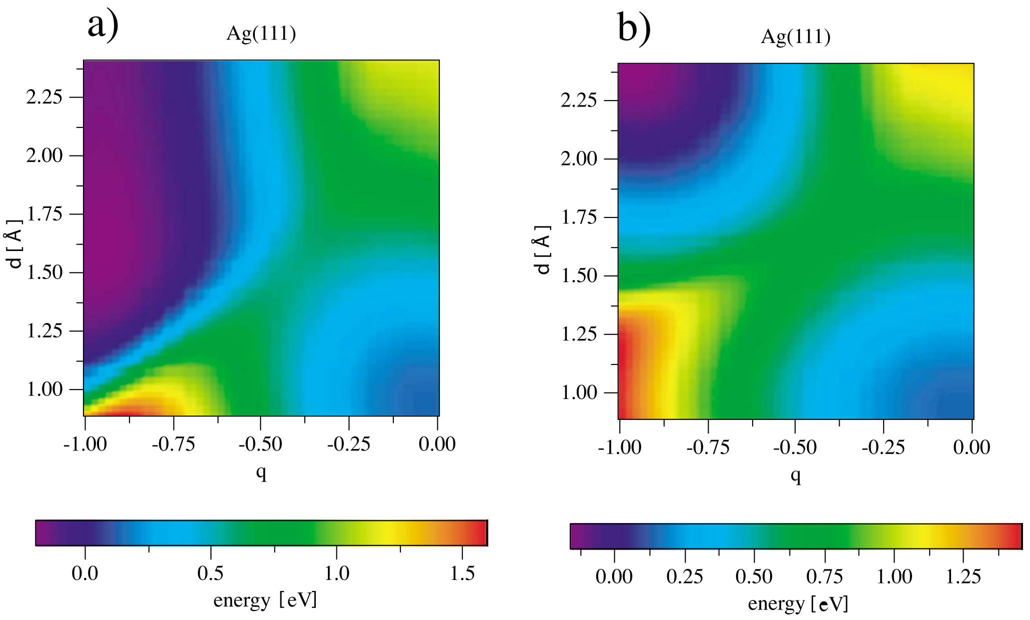

FIG. 4. (Color online) Free-energy surface for hydrogen adsorption on Ag(111) with (a) a constant and (b) a variable energy of reorganization.

with the surface and lowers the overall energy a little. Compared with the results of computer simulations,[23,30] the minimum obtained for constant λ is somewhat too close to the surface, and the surface with variable λ seems more realistic. Fortunately, the two energies of activation are quite close; as we shall see below, the trend in the activation energies between various metals is exactly the same for both assumptions about λ. In the rest of this paper, we shall give the energies of activation for both cases, but we shall only show surfaces calculated for a variable λ.

As the system passes from the solvated proton to the adsorbed hydrogen atom the occupancy of the hydrogen orbital increases gradually from zero to unity; Fig. 5 shows a corresponding plot. In accord with Fig. 4(b) it indicates that the reaction path goes almost straight from $q=-1$, $d=2.3$ Å to $q=0$, $d=0.9$ Å.

The free-energy surfaces for the other four metals are shown in Fig. 6; the energies of activation are shown in Table II. To facilitate the interpretation, the densities of states of the d bands are given in Fig. 7. First we note that the energies of activation calculated with a variable reorganization energy are about 0.1 eV higher than those obtained with a constant λ. This difference is smaller than the uncertainty in the experimental values for the rate constants, which vary by one to four orders of magnitude.[10] Also, with both approaches we obtain exactly the same trend.

The energy of activation is highest for cadmium, because its d band lies between −10 and −8 eV below the Fermi level and is quite narrow. Therefore, in spite of the relatively high coupling constant, it has no catalytic effect. Indeed, if we switch off the coupling by setting $|V|^2=0$, we obtain exactly the same activation energy. Of course, in pure DFT-based calculations it is not possible to switch off an interaction at will; this is an advantage of our semi-analytic approach. Experimentally, hydrogen evolution occurs with roughly the same speed on metals such as Cd, Hg, Pb, Tl, and In, all of which have d bands that lie too low to affect the activation energy. Therefore, on these metals the reaction is dominated by the sp band, whose interaction does not seem to vary much between the metals.

On the three coin metals Cu, Ag, and Au the reaction has roughly the same energies of activation. This is due to a compensation effect: the interaction $|V|^2$ with the d band increases down the column of the periodic table, which lowers the energy of activation. On the other hand, the energy of the adsorbed hydrogen increases in the same order (see Table I); therefore, the reaction free energy for the adsorption rises, which in turn raises the activation energy. The increase in the adsorption energy down the column is very well explained in the paper by Hammer and Nørskov.[24] On all three metals, the d band lies well below the Fermi level. Therefore, both the

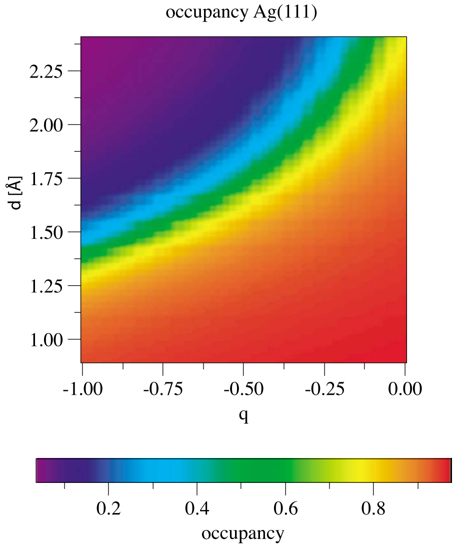

FIG. 5. (Color online) Occupancy of the hydrogen 1s orbital on Ag(111).

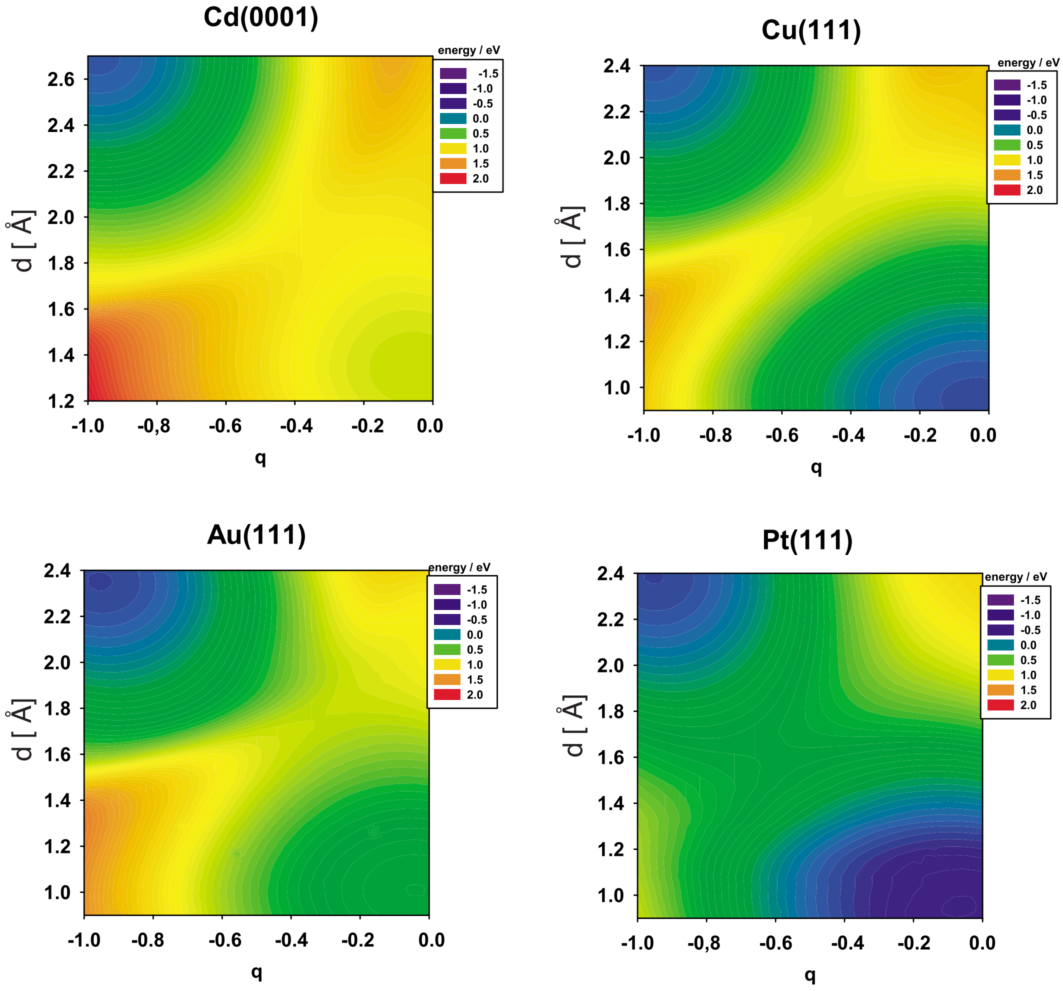

FIG. 6. (Color online) Free-energy surfaces for hydrogen adsorption at Cd(0001), Cu(111), Au(111), and Pt(111).

bonding and the antibonding part of the hydrogen DOS caused by the interaction with the *d* band are filled, so that the *d* band does not contribute much to the adsorption bond, which is therefore dominated by the interaction with the *sp* band. In fact, the interaction with the *d* band weakens the adsorption bond, because the hydrogen orbital must be orthogonalized with respect to the *d* orbitals. The required orthogonalization energy increases with the extension of the *d* states,[17] and is roughly proportional to $|V|^2$.

The experimental values for the reaction rates vary by several orders of magnitude, with older experiments giving lower values than more recent ones. As has been discussed before,[10] there has been significant progress in the surface treatment of the coin metals during the last two decades. Therefore, the more recently measured rate, which are roughly the same on the three metals, seem more trustworthy, and these are in line with our calculated results.

Of the metal considered, platinum is the only one whose *d* band extends over the Fermi level. Its interaction with hydrogen is strong, and therefore it has by far the lowest activation energy. At the equilibrium electrode potential, the energy of the adsorbed hydrogen is lower than that of the solvated proton. Therefore adsorption sets in at potentials above the hydrogen evolution, so that one speaks of strongly

TABLE II. Energies of activation for hydrogen adsorption on various metals. First row: variable energy of reorganization λ; second row: constant λ.

Metal	Cd	Cu	Ag	Au	Pt
λ variable	0.93	0.71	0.71	0.70	0.30
λ constant	0.83	0.61	0.57	0.63	0.0

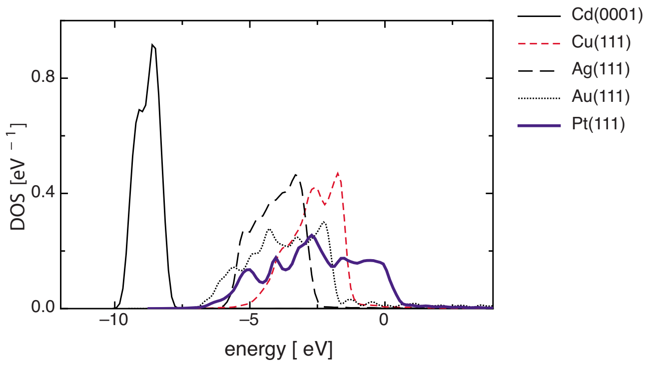

FIG. 7. (Color online) Surface *d* band DOS of the metals considered.

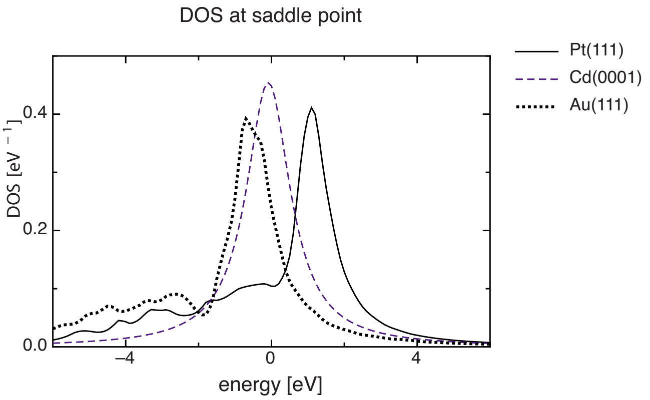

FIG. 8. (Color online) Hydrogen DOS at the saddle point.

adsorbed hydrogen, or sometimes of hydrogen deposited at underpotential (H_{upd}). However, there is convincing experimental evidence that this is not the species that takes part in hydrogen evolution,[25] but that the intermediate is a more weakly adsorbed species. So our calculations correspond to the deposition of the strongly adsorbed species. Experimentally, this reaction is so fast that it has not been possible to measure its rate. This is in line with the very low energy of activation that we obtained.

As we have discussed in detail elsewhere,[8,18] a good catalyst broadens the DOS of the reactant as it passes the saddle point. This effect lowers the electronic energy, and at the same time the partial discharge increases the solvation. Figure 8 shows the hydrogen density of states at the saddle point for Cd, Au, and Pt. For Cd, the DOS is only broadened by the *sp* band, while the DOS at platinum and at Au are widened in the region of their *d* bands, the effect being somewhat larger for Pt. The saddle points occur for different occupancies at the three metals. On Pt, the orbital is about half filled ($\langle n \rangle = 0.55$), while for Au and Cd the occupancy is much higher (for Cd: $\langle n_a \rangle = 0.75$ and for Au $\langle n_a \rangle = 0.79$), because the adsorption of the proton is uphill. The significant broadening of the DOS on Au shows, that this metal would be quite a good catalysts, if the energy of the adsorbed hydrogen were not so high.

In our model, a change in the electrode potential affects the energy of the solvated proton [see Eq. (8)], since the energy zero has been chosen as the Fermi level of the metal. Thus, we are able to calculate free-energy surfaces and energies of activation for various overpotentials η. For small changes in potential, the change in activation energy is proportional to the change $e_0 \eta$ in the free energy of the reaction. The constant of proportionality is the transfer coefficient α. It is not surprising that the exact value of α depends on the model that we use for the energy of reorganization. For the systems and models investigated, we obtain values for α in the range of 0.3 to 0.7, which is also the range of experimental values. For outer sphere electron transfer, the transfer coefficient is always close to 1/2, but for proton and ion transfer, a wider range is expected.[25]

V. DISCUSSION AND CONCLUSIONS

Hydrogen evolution is the best investigated electrochemical reaction and is considered as a prototype for electrocatalysis. However, in spite of decades of efforts, there was no real understanding of hydrogen electrocatalysis, or of any other electrochemical reaction, until a few years ago. All that existed were a few correlations, the *volcano plot* between the reaction rate and the energy of hydrogen adsorption being the best known. However, if one discards all metals that are covered by oxide films from the volcano plot, the experimental evidence for the correlation disappears. This is true both for the older version of Trasatti[26,27] and the more recent one by Norskøv *et al.*[11] (see also the comment by Schmickler and Trasatti[28] on the latter paper).

A proper understanding cannot be based on correlations, nor can it be obtained by performing DFT calculation for a large number of cases—it requires a theory. So in this work, we have linked a theory for electrocatalysis proposed by two of us[8,9] with DFT calculations and applied it to the hydrogen evolution reaction, focusing on the adsorption of the proton, which is the rate-determining step in the systems investigated. Our method allowed us to calculate the free energy of the reaction as a function of the distance of the reactant from the surface and of the solvent coordinate. In all cases we obtained two minima corresponding to the proton and the adsorbed hydrogen atom, separated by a saddle point, from which we determined the energy of activation. As pointed out above, our results are well in line with the experimental data. A more quantitative comparison can be made by estimating the pre-exponential factor of the quantity measured by experimentalists, the standard exchange current density j_{00}, which is proportional to the rate constant at equilibrium. The pre-exponential factor is given by $A = Fc_s^0/\tau \approx 10^5$ A cm^{-2}, where F is Faraday constant, c_s^0 is the surface concentration of the proton, i.e., the concentration in roughly the first 5 Å adjacent to the electrode, and $\tau \approx 10^{11}$ s^{-1} is a typical reorientation time for water. As shown in Table III, our calculated free energies of activation have about the correct order of magnitude and, somewhat surprisingly, the uncertainty in experimental data is about the same as that of our model.

TABLE III. $-\log_{10} j_{00}$ for hydrogen evolution; upper row: values obtained from Table II; lower row: range of experimental values (Ref. 10). The standard exchange current density j_{00} is proportional to the rate constant at the equilibrium potential.

Metal	Cd	Cu	Ag	Au	Pt
This work	9.4–11.2	5.6–7.3	4.9–7.3	6.0–7.1	−5–0.2
Experimental values	10–12	5–6	5–7.8	5.4–6.8	

In a recent publication[10] we had explained hydrogen catalysis by model calculations based on the position of the metal *d* band and average interaction constants $|V|^2$. While our present work does not invalidate the previous one, it adds much more details and allows calculations for a specific electrode potential. In particular, it shows that the free energy of adsorption plays an important role as well, a higher more endothermic adsorption energy being detrimental for catalysis. This can be clearly seen in the case of gold. In so far the ascending branch of the volcano plot with positive adsorption energies has some justification even though the interaction strength and the position of the *d* band do not always correlate with the adsorption energy. A low highly exothermic adsorption energy might also be thought to be unfavorable, since it impedes the desorption that is involved in the second step of the hydrogen evolution reaction. However, strongly adsorbing metals such as platinum and palladium usually offer more than one adsorption site, and the less strongly adsorbed atoms will participate in the reaction if this is more favorable.

The purpose of this work was to examine hydrogen electrocatalysis quantitatively, and we believe that our results are encouraging. Our theory incorporates all the important properties of the metal and therefore explains their relative catalytic activities well. Here, we have only considered pure metals, but with the same method, we can consider nanostructures such as metal overlayers, islands, or steps, as well, and our first results for such systems[13] are promising. The weakest part of our model is the solvent, which is characterized only by the reorganization and the solvation energy. For a full understanding of hydrogen evolution we require a more detailed model for the solvent such as may be obtained from molecular dynamics or similar methods.[29,30] However, as long as one is interested only in catalysis, the present treatment is sufficient.

The most popular alternatives to our approach are based purely on DFT computation. A principal problem is always the inclusion of the electrode potential, although some useful approximations exist.[31,32] Molecular dynamics has been tried with some success on Pt,[30] but a proton transfer was observed only for extremely high fields. An easy estimate shows that for typical system sizes and simulation times—surface smaller than 100 Å^2, 10 ps—the transition of one proton corresponds to a current density of about 1×10^6 A cm^{-2}, which is four orders of magnitude higher than the experimentally accessible range. This estimate also shows that this approach would be impossible for worse catalysts such as silver or copper, and not to mention cadmium.

Medium-sized DFT calculations, which do not explicitly treat charge transfer, are useful to determine the thermodynamics of reaction steps, and much useful work, too numerous to list, has been done in this way. Several attempts have been made to calculate proton or electron transfer steps explicitly, but they all suffer from the relatively small system size, the difficulty to define the electrode potential, and to incorporate counter charges in the solution when the electrode is charged. The most comprehensive computational study to date has been performed by Skulason *et al.*[33] for hydrogen evolution on Pt(111), who modeled the solution by a bilayer of water with up to four protons interspersed. Of course, the pH of the model solution is extremely high, and there is little water, but this ambitious work is at the limit of what can presently been done. The authors calculate activation energies and attempt to correct for the fact that the electrode potential changes as a proton is adsorbed from the solution. For the adsorption of the first hydrogen atom, they obtain an activation energy compatible with our values. In an earlier work, Ohwaki and Yamashita[34] studied proton transfer from a Zundel ion $H^+(H_2O)_2$ to Pt(111) and Ag(111). In contrast to us, they obtained the same order of magnitude for the activation energy on both metals. We believe that the main value of such computationally expensive calculations is the possibility to learn more details about the role of the solvent.

Our approach is not limited to hydrogen evolution; with appropriate changes it can be applied to other electrochemical reactions as well. The application to the adsorption of other cations of the type $A^+ + e^- \rightarrow A$ is straightforward, adsorption of anions will require a modification of Eq. (7) for the exchange-correlation correction, since the valence orbital of the ion is filled. A similar approach can be used for the reactions of molecules; in this case the valence orbital is a molecular orbital. Indeed, the general principles of such reactions have already been investigated by two of us.[8,9]

In summary, in this work we have presented a unique approach to hydrogen electrocatalysis, which provides an understanding in terms of the electronic properties of the electrode. Explicit model calculations performed for five metals reproduced well the observed experimental trends, and even gave a good estimate for the reaction rates.

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APPENDIX: DETAILS OF DFT CALCULATIONS

All calculations were performed using the dacapo code.[35] This utilizes an iterative scheme to solve the Kohn-Sham equations of density-functional theory self-consistently. A plane-wave basis set is used to expand the electronic wave functions, and the inner electrons were represented by ultrasoft pseudopotentials,[36] which allow the use of a low-energy cutoff for the plane-wave basis set. An energy cutoff of 400 eV, dictated by the pseudopotential of each metal, was used in all calculations. The electron-electron exchange and correlation interactions are treated with the generalized gradient approximation in the version of Perdew *et al.*[37] The Brillouin-zone integration was performed using a $16 \times 16 \times 1$ **k**-point Monkhorst-Pack grid[38] corresponding to the 1×1 surface unit cell. The surfaces were modeled by a 3

×3 supercell with four metal layers and six layers of vacuum; calculations with a 2×2 supercell, five metal layers, and ten layers of vacuum gave practically the same results. Dipole correction was used to avoid slab-slab interactions.[39] The first two top layers were allowed to relax, while the bottom two layers were fixed at the calculated next-neighbor distance. The optimized surfaces (pre-relaxed) in the absence of the hydrogen atom were used as input data to carry out the calculations to study the hydrogen desorption. For each systems, we performed a series of calculations for a single atom adsorbed on a hollow site, and varied its separation from the surface. The pre-relaxed surface was kept fixed while the H was allowed to relax in the *xy* coordinates during these calculations. At each position we calculated the adsorption energy and the DOS projected onto the 1*s* orbital of hydrogen.

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