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PAPER

# A model for the Heyrovsky reaction as the second step in hydrogen evolution

E. Santos,<sup>ab</sup> P. Hindelang,<sup>b</sup> P. Quaino<sup>bc</sup> and W. Schmickler<sup>\*b</sup>

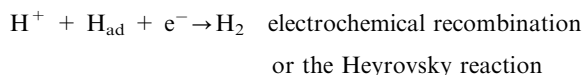
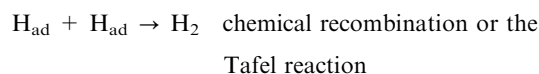
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On a number of electrodes the second step in hydrogen evolution is the reaction of a proton with an adsorbed hydrogen intermediate to form a molecule, which is also known as the Heyrovsky reaction. We have developed a model Hamiltonian for this reaction, which for concrete applications requires extensive calculations on the basis of density-functional theory. Explicit results are presented for a Ag(111) electrode. The rate-determining step is electron transfer to the proton that approaches the electrode from the solution. At the saddle point for this reaction the adsorbed hydrogen atom has moved a little away from the surface in order to reduce the repulsion of the product molecule. Electron transfer to the proton occurs when the distance between the two particles is close to the bond distance of the hydrogen molecule.

## 1. Introduction

Hydrogen evolution on metal electrodes from acid solutions proceeds in two steps. The first is always the adsorption of an intermediate hydrogen atom according to:  $\text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ad}}$ , which is also known as the Volmer reaction. In recent years this step has been the focus of a large number of theoretical studies, e.g. ref. 1–9, many of them based on density-functional theory (DFT). For the second step there are two possibilities:



The chemical recombination can be investigated by standard DFT and thus poses no particular challenge, particularly since Gohda *et al.*<sup>10</sup> have recently shown that it is only little affected by the presence of water on the surface. Therefore, its energetics will be very similar to the corresponding reaction in the vacuum, where it is well studied. In contrast, the electrochemical recombination involves an electron transfer and desolvatisation of the proton, and therefore cannot occur in vacuum. Because of the strong solvation of the proton, a direct simulation by DFT is difficult, if not impossible, and we are only aware of two studies by the same group where it has been included.<sup>1,2</sup> This extensive numerical calculation was

performed for the Pt(111) surface, where the second step is probably the chemical recombination.

By their very nature, DFT calculations can only be performed for specific systems, and since they are wholly numeric they do not give as much insight as proper theories. Therefore, in our group we have developed our own approach for the investigation of electrochemical processes: we set up model Hamiltonians appropriate to the reaction under study; these contain a certain number of interaction parameters, which we obtain by DFT. During the last few years, we have successfully applied our method to hydrogen evolution, focusing on the Volmer step.<sup>11,12</sup> Here, we will study the electrochemical recombination; since this involves two hydrogen atoms, it requires an extension of our model Hamiltonian and more extended DFT calculations to obtain the interactions. We will apply our model to hydrogen evolution on Ag(111), because on this surface the reaction follows the Volmer–Heyrovsky course.<sup>13,14</sup>

Before we present our own work, we would like to remind our readers of the extensive work of the Soviet school<sup>15</sup> on hydrogen evolution of the 1960s and 70s. Of course, this was too early to treat catalytic effects, but some of the concepts developed at that time can help to understand qualitative aspects, as we shall point out below.

## 2. The model Hamiltonian

The reverse of the Heyrovsky reaction has the nature of a bond breaking electron transfer, for which Santos *et al.*<sup>16,17</sup> have developed a formalism, the so-called SKS Hamiltonian. The original formulation was for the case in which the molecule separates into two equivalent atoms, but it has recently been extended to the more general case.<sup>18</sup> In the

<sup>a</sup> Facultad de Matemática, Astronomía y Física, IFEG-CONICET, Universidad Nacional de Córdoba, Córdoba, Argentina

<sup>b</sup> Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany. E-mail: Wolfgang.Schmickler@uni-ulm.de

<sup>c</sup> PRELINE, Universidad Nacional del Litoral, Santa Fe, Argentina

Heyrovsky reaction, the two hydrogen atoms are not equivalent, but the situation is a little simpler than that discussed in the latter article. Firstly, as we shall show below, the reaction takes place so close to the electrode that spin polarization plays no role. Therefore, we may neglect spin complications. Secondly, the hydrogen atom that at first is in the adsorbed state stays uncharged, so that its interaction with the solvent is weak and can be neglected.<sup>10</sup> These two facts simplify the model Hamiltonian, which we present below in three parts. We denote the two hydrogen atoms as  $H_a$  and  $H_b$ — $H_a$  being initially adsorbed and  $H_b$  approaching in the form of a proton—and give their 1s orbitals the corresponding indices  $a$  and  $b$ . The Hamiltonian for the two atoms interacting with each other is then:

$$H_{\text{mol}} = \varepsilon_a n_a + \varepsilon_b n_b + \beta c_a^+ c_b + \beta c_b^+ c_a \quad (1)$$

Here  $\varepsilon$  denotes the energy of an atomic orbital,  $n$  is the occupation operator, and  $c^+$  and  $c$  are creation and annihilation operators. The interaction  $\beta$  between the two atoms has been taken as real, which can be done without loss of generality. Both atoms interact with the metal, whose electronic states we label with an index  $k$ , which runs both over the sp and the d band. We write the corresponding interaction terms as:

$$H_{\text{met}} = \sum_k \{ \varepsilon_k n_k + (V_{a,k} c_k^+ c_a + V_{b,k} c_k^+ c_b + \text{h.c.}) \} \quad (2)$$

where h.c. stands for the hermitean conjugate.

Finally we specify the terms for the solvent and any vibrational modes that interact with the electron exchange. They are represented as a phonon bath that interacts linearly with the charge on the atoms. Only the approaching proton  $H_b$  interacts with the solvent. Therefore the corresponding terms are:

$$H_{\text{sol}} = \frac{1}{2} \sum_{\nu} \hbar \omega_{\nu} (q_{\nu}^2 + p_{\nu}^2) + (1 - n_b) \sum_{\nu} \hbar \omega_{\nu} g_{\nu} q_{\nu} \quad (3)$$

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

As long as all interacting modes are classical, they can be represented by a single, effective solvent coordinate  $q$ .<sup>20,21</sup> It is convenient to normalize this coordinate in the following way: when the state of the solvent is represented by  $q$ , it would be in equilibrium with an atom  $H_b$  which carries a charge of  $-q$ . We shall use this one-dimensional representation in the following.

The sum of the three terms  $H = H_{\text{mol}} + H_{\text{met}} + H_{\text{sol}}$  constitutes our model Hamiltonian. The corresponding Green's function and the resulting density of states are given in the Appendix. Here we summarize the important system parameters. Generally the metal substrate contains both an sp and a d band. We take the coupling constants to the d band as independent of the energy and call them  $V_a$  and  $V_b$ . They give rise to chemisorption functions:

$$\Delta_a(\varepsilon) = |V_a|^2 \pi \rho_d(\varepsilon) \quad \Delta_b(\varepsilon) = |V_b|^2 \pi \rho_d(\varepsilon) \quad (4)$$

where  $\rho_d(\varepsilon)$  is the density of states of the metal d band. These functions have the meaning of an energy-dependent broadening of the orbitals. The corresponding level shifts are obtained by a Hilbert transform:<sup>22</sup>

$$\Lambda_i(\varepsilon) = \frac{1}{\pi} \mathcal{P} \int \frac{\Delta_i(\varepsilon')}{\varepsilon - \varepsilon'} d\varepsilon' \quad (5)$$

where  $i = a, b$ , and  $\mathcal{P}$  denotes the principal part. The sp band will be represented by a semi-elliptical band of width 12.5 eV centered at  $-2.5$  eV with respect to the Fermi level  $E_F$ ; we set  $E_F = 0$  throughout this article. Since this band is very wide, its exact position has no effect on the results. The interaction with the sp band will thus be represented by:

$$\Delta_{\text{sp}}^i = \Delta_0^i \rho_{\text{sp}}(\varepsilon) \quad (6)$$

The explicit form for the semielliptical band is given in ref. 12.

Other important parameters are the energy levels  $\varepsilon_i$  of the two atoms, and the interaction  $\beta$ . Of the two atoms, the adsorbed atom  $H_a$  never acquires charge, and therefore we can neglect its interaction with the solvent. In contrast, atom  $H_b$  is initially a proton, and thus interacts strongly with the solvent. For the corresponding energy of reorganization we have assumed a value of  $\lambda = 3$  eV. As detailed in ref. 12, we assume that its value right at the position of the adsorbed atom is lower by a factor of two, and that the decay occurs over a distance of 1.5 Å. This decay of the reorganization energy is also supported by calculations in a continuum model.<sup>23</sup>

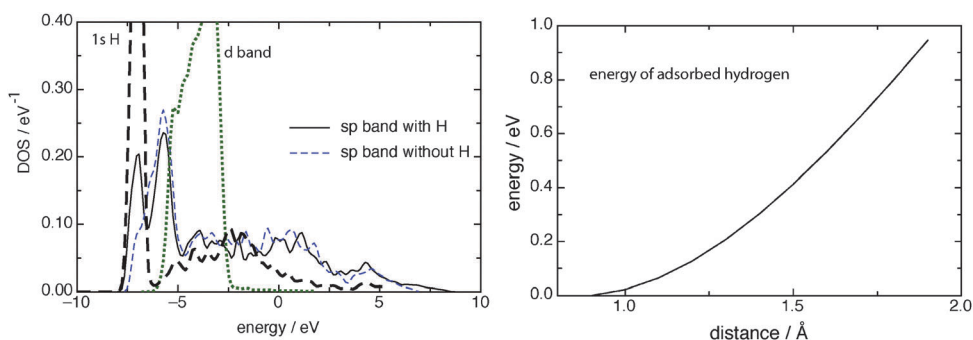
The technical details of the DFT calculations, which complement our theory, are given in the Appendix. Here we note that the calculations for the two hydrogen atoms were performed with spin polarization to verify that indeed it does not play a role in the reaction region.

### 3. Preparatory studies

#### 3.1 Bonding of the adsorbed hydrogen atom to Ag(111)

Since the adsorbed hydrogen atom is detached during the reaction, its bonding to the surface plays an important role. Therefore, in Fig. 1 we show the densities of states of the adsorbed H atom and the bands at the surface of Ag(111). The d band of silver lies well below the Fermi level; it forms a bonding and an antibonding state with the hydrogen 1s orbital. Both of them are filled, so that they play no role in the bonding of the hydrogen atom, a fact that has been known for some time (see *e.g.* ref. 24). The d band is practically not affected by the adsorption, therefore we show its density only for the free surface. The sp band, however, binds strongly to the adsorbate; it forms a peak which overlaps with the 1s orbital of hydrogen. Thus, the sp band does more than just induce a broadening of the hydrogen orbital.

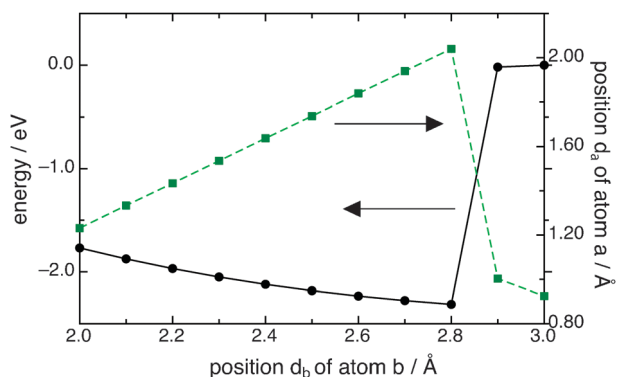
The equilibrium position of the adsorbed atom is in the fcc hollow site at a distance of about 0.9 Å from the surface. When the adsorbed atom is pulled away from the surface, letting it move freely in the direction parallel to the surface, its energy at first rises slowly, because of the long range of the sp orbitals (see Fig. 1). This fact will become important when we consider the Heyrovsky reaction.



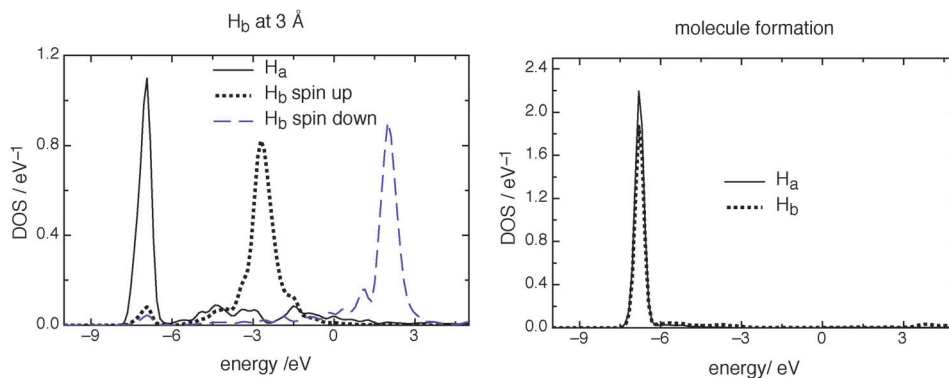
**Fig. 1** Densities of states of Ag(111) and of the adsorbed hydrogen atom (left) and energy of the adsorbed atom as a function of the distance from the surface (right).

### 3.2 Approach of a hydrogen atom

In the Heyrovsky reaction a *proton* approaches the adsorbed hydrogen atom, gets discharged, and forms a bond with the other atom. As a preliminary study, it is instructive to let a hydrogen *atom* approach the adsorbed atom, and let the latter move freely during the approach. The result is shown in Fig. 2: as soon as the approaching atom is at a distance of about 2.8  $\text{\AA}$ , the other atom jumps to a distance of about 2  $\text{\AA}$  and forms a molecule; at the same time the energy drops by about 2.3 eV. This is significantly lower than the binding energy of about 4.55 eV, since the adsorption energy of  $\text{H}_a$  to silver,



**Fig. 2** Energy change as the hydrogen atom  $\text{H}_b$  approaches the adsorbed atom  $\text{H}_a$  (left axis) and position  $d_a$  of  $\text{H}_a$  (right axis).



**Fig. 3** Densities of states of the hydrogen atoms. Left: when  $\text{H}_b$  is at 3  $\text{\AA}$  from the surface; right: bonding orbital when  $\text{H}_b$  is at 2.8  $\text{\AA}$  and the molecule has formed.

### 3.3 Spin polarization

Although spin polarization plays no role in the critical region where the reaction takes place, it is of interest to see how the interaction of the approaching atom  $H_b$  with the surface and with the other atom  $H_a$  affects its spin orbital. A few typical situations are shown in Fig. 4. When the adsorbed atom  $H_a$  is at its equilibrium position, and  $H_b$  far from the surface, the latter is spin polarized. At  $d_b = 3 \text{ \AA}$  one spin orbital lies mainly above the Fermi level, the other one mainly below. Both have a small peak near  $-7.5 \text{ eV}$  which overlaps with the main peak in the DOS of the adsorbed atom. When  $H_b$  approaches to  $2.7 \text{ \AA}$ , both spin orbitals are somewhat broadened because of the interaction with the metal surface; at the same time the overlap with the adsorbed atom becomes stronger, and the corresponding peak grows. At  $2.4 \text{ \AA}$  spin polarization has disappeared, there is only one single DOS, and the interaction with the adsorbate has become even stronger. Fig. 4d shows the spin polarization as a function of the position  $d_b$ . When the atom  $H_a$  is further away from the surface, spin polarization of  $H_b$  disappears at larger distances. Obviously, both the interactions of  $H_b$  with the surface and with the other atom affect the spin polarization.

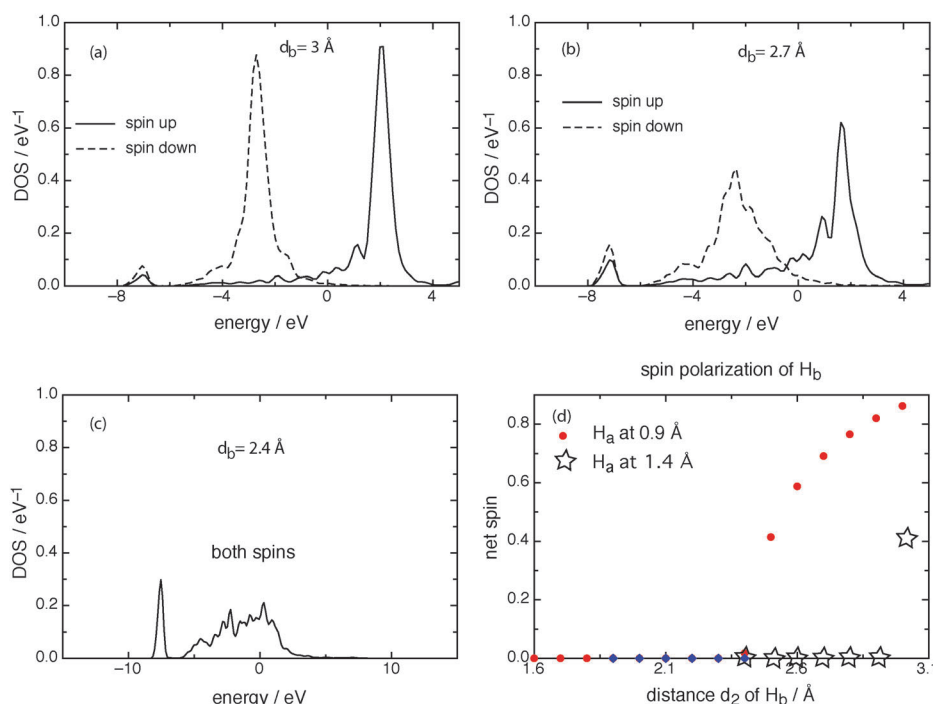
### 3.4 Determining the system parameters

There are five important parameters to fit: the interaction constants  $|V_a|^2$  and  $|V_b|^2$  of the two atoms with the d band, their energy levels  $\varepsilon_a$  and  $\varepsilon_b$ , and the interaction  $\beta$ ; all of them depend on the positions of the two particles. The parameters  $V_a$  and  $\varepsilon_a$  characterize the interaction of the originally adsorbed atom  $H_a$  with the surface. They should only depend on the position of  $H_a$ , and have already been obtained from

calculations with a single atom at various distances in our previous publication,<sup>12</sup> so we have used those values. The other three parameters have been calculated by fitting the densities of states of our model (see Appendix) to those obtained from DFT. As we discussed in our previous work<sup>12</sup> it is not possible to determine the interaction constants  $\Delta_{sp}^a$  and  $\Delta_{sp}^b$  by fitting as well, so for these we used constant values; the former is known from our previous work, to the other we shall return below.

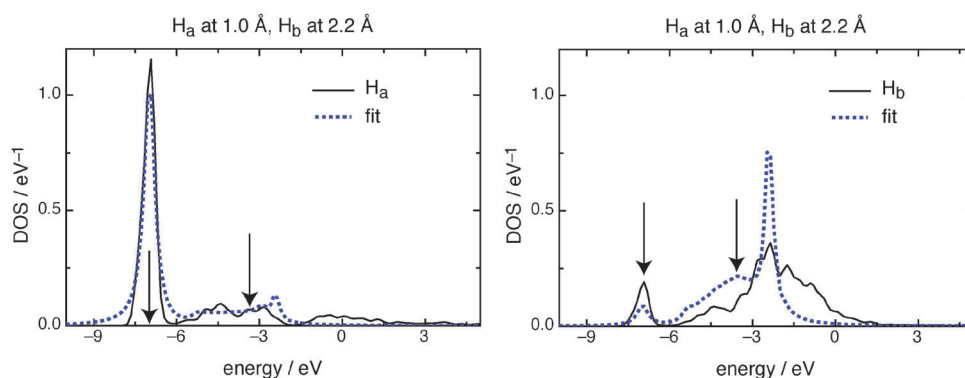
To obtain the parameters  $V_b$ ,  $\varepsilon_b$  and  $\beta$ , we performed DFT calculations for various distances of the two atoms from the surface, leaving them free to move in the plane parallel to the surface, and obtained the densities of states for both atoms. These were then used as a basis for fitting the constants; thus, for each combination of distances the parameters are fitted to the DOS of both atoms. As we discussed in our work on proton transfer,<sup>12</sup> it is not possible to obtain the interaction  $\Delta_{sp}^b$  also by fitting—four parameters is simply too much. However, one can get a good estimate of  $\Delta_{sp}^b$  from the width of the lower peak in the DOS of atom  $H_b$  (see Fig. 5), which lies below the d band. This gives us an average value of  $\Delta_{sp}^b = 0.3 \text{ eV}$  for all situations. This value is somewhat lower than the value of  $0.7 \text{ eV}$  we obtained for proton adsorption. The presence of atom  $H_a$  screens atom  $H_b$  from the sp band, and decreases its interaction. Fig. 5 also shows the quality of our fit; generally, it reproduces the DOS of the adsorbed atom  $H_a$  very well, and for the more remote atom  $H_b$  the main features are produced well.

As an example, Fig. 6 shows the parameters obtained for the case when atom  $H_a$  is kept fixed at a distance of  $1 \text{ \AA}$ , and the position  $d_b$  of atom  $H_b$  is varied. As expected, the interaction  $\beta$  between the two hydrogen atoms decreases strongly with the separation. The interaction  $|V_b|^2$  with the d band at first increases slightly, and then falls off. We attribute the lowering

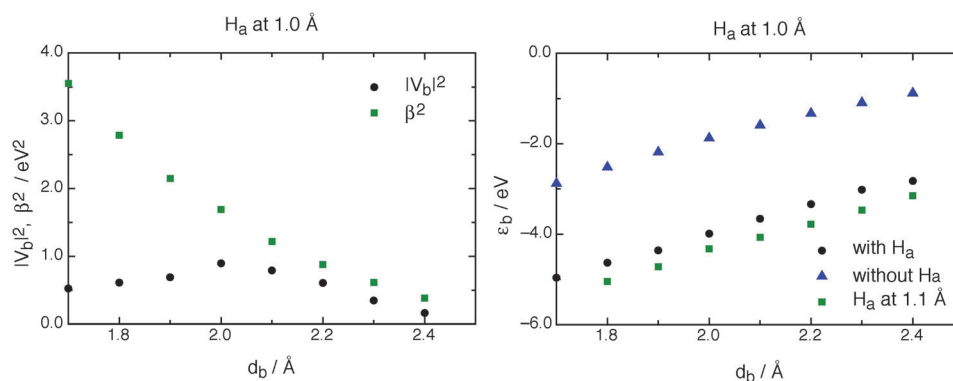


**Fig. 4** Densities of states of atom  $H_b$  for various distances when  $H_a$  is at  $0.9 \text{ \AA}$ . (a)  $d_b = 3 \text{ \AA}$ , (b)  $d_b = 2.7 \text{ \AA}$ , (c)  $d_b = 2.4 \text{ \AA}$ . (d) Spin polarization of atom  $H_b$  for two positions of  $H_a$ .





**Fig. 5** Densities of state for the two atoms obtained from DFT and the best fits from our model. Left: atom  $H_a$ , right: atom  $H_b$ ; the two atoms were positioned at distances of 1.0 Å and 2.2 Å from the surface, respectively. The arrows indicate the positions of the bonding and antibonding orbitals of the molecule as calculated from eqn (19) and (20) in ref. 18.



**Fig. 6** Parameters for atom  $H_b$  obtained when  $H_a$  is at a distance of 1 Å from the surface. We show  $\beta^2$  rather than  $\beta$  so that it can be plotted in the same figure as  $|V_b|^2$ .

at short distances again to the shielding of the interaction by the atom  $H_a$ . At distances larger than 2.2 Å it is very similar to the interaction in the absence of  $H_a$ .

The energy level  $\epsilon_b$  decreases as the atom approaches the surface, an effect that has been well known since the first model calculations on jellium.<sup>25</sup> However, in the presence of the other hydrogen atom the effect is stronger than on the bare surface. Obviously, the interaction between the two atoms leads to a further lowering of the level  $\epsilon_b$ . A little thought shows that such an effect has to be expected. Our model Hamiltonian does not account for overlap between the two atoms, and hence the two levels must be considered as pertaining to orthogonalized orbitals whose energies are modified by the interaction. The effect is consistent for all positions of  $H_a$ . As an example, Fig. 6 shows the values when  $H_a$  is at 1.1 Å. In this case,  $\epsilon_b$  lies a little lower since  $H_b$  is now a little closer to the other atom, but the slope is the same.

## 4. Energetics of the Heyrovsky reaction

### 4.1 Combining DFT energies with our model

Within our model Hamiltonian the energy of the two reactants is:

$$E_{\text{model}}(d_a, d_b, q) = \int_{-\infty}^0 \epsilon \rho_a(\epsilon) d\epsilon + \int_{-\infty}^0 \epsilon \rho_b(\epsilon) d\epsilon + \lambda q^2 + 2\lambda q \quad (7)$$

Here,  $d_a$  and  $d_b$  are the positions of  $H_a$  and  $H_b$ . The densities of states  $\rho_a(\epsilon)$  and  $\rho_b(\epsilon)$  of the two atoms are obtained from Green's functions given in the Appendix. They depend explicitly on  $q$ , and implicitly on  $d_a$  and  $d_b$  through the system parameters. The last two terms pertain to the solvent, and this simple form has been obtained by the normalization of the solvent coordinate.

Eqn (7) suffers from the usual deficiency of Anderson–Newns type models:<sup>22,27</sup> it neglects exchange and correlation effect. In a recent publication<sup>12</sup> we have shown for the case of a simple proton transfer, how we can correct for this using the energies calculated from DFT. Here we shall use an equivalent method for the Heyrovsky reaction.

For this purpose we first consider the case when both hydrogen atoms are uncharged. In this case, the electronic energy of the atoms is given exactly by DFT, and is defined as the energy of the system minus that of the bare silver surface. We call this energy  $E_{\text{DFT}}(d_a, d_b)$ . Within our model, this corresponds to the solvent configuration  $q = 0$ . Therefore in this case the correction is:

$$\Delta E(d_a, d_b) = E_{\text{DFT}}(d_a, d_b) - \int_{-\infty}^0 \epsilon \rho_a(\epsilon) d\epsilon + \int_{-\infty}^0 \epsilon \rho_b(\epsilon, q = 0) d\epsilon \quad (8)$$

where we have indicated that only atom  $H_b$  interacts with the solvent. We would like to obtain a correction valid for all

values of  $q$  in the relevant range. The energy of the two atoms can be split into the energy  $E_a(d_a)$  of atom  $H_a$  in the absence of atom  $H_b$ , and the energy  $E_b(d_a, d_b)$  of atom  $H_b$  including its interaction with  $H_a$ . Only the latter part will vary with  $q$ . For  $q = 0$  we can calculate  $E_a$  and  $E_b$  both from DFT and from our model; we need the difference:

$$\Delta E_b(d_a, d_b, q = 0) = E_{b,\text{DFT}}(d_a, d_b) - E_{b,\text{model}}(d_a, d_b) \quad (9)$$

When  $H_b$  is fully ionized, *i.e.*  $\langle n_b \rangle = 0$ , both its electronic energy and its interaction with  $H_a$  vanish. In this case our model also gives the correct result, and the correction to  $E_b$  vanishes. For  $\langle n_b \rangle = 1$ , eqn (9) gives the full correction. In the spirit of ref. 12 we interpolate linearly between these two limiting cases and define the correction:

$$\Delta E_b(d_a, d_b) = \Delta E_b(d_a, d_b, q = 0) \langle n_b \rangle \quad (10)$$

In this way we extrapolate our DFT results, which are valid for  $q = 0$ , to all values in the range  $-1 \leq q \leq 0$ . We note in passing that DFT itself is partially based on interpolations between well-defined limiting cases; therefore we may expect eqn (10) to be a good starting point for this hitherto unexplored reaction.

Finally, we have to introduce the interactions of the proton that are not contained in the model Hamiltonian. Like in all Marcus-type theories,<sup>26</sup> the Hamiltonian contains only the interaction with the slow solvent modes, the interaction with the fast modes is missing. In addition, there is generally an electrostatic potential drop between the electrode and the solution. The missing energy can be obtained from the following consideration: in our model, the energy of the proton in its initial state is  $-\lambda$ ; from thermodynamics, we know that it should be equal to one half of the free energy of the  $H_2$  molecule at standard conditions.<sup>12,19</sup> This gives a value of  $E_p = -16.05$  eV, so at the equilibrium potential the missing part is  $E_p - \lambda$ . Application of an overpotential  $\eta$  adds an additional term  $-e_0\eta$ . When the proton is fully discharged, these interaction terms vanish. Using a linear interpolation, we obtain for the missing term:

$$V_f = (1 - \langle n_b \rangle)(E_p + \lambda - e_0\eta) \quad (11)$$

This is the same term that we had previously introduced in our model for proton adsorption.<sup>12</sup>

## 4.2 Free energy surfaces and activation energy

With the procedure presented above we are able to calculate the energy as a function of the three coordinates  $d_a$ ,  $d_b$ ,  $q$ . Like in the Marcus theory, the use of a single solvent coordinate implies a thermal average over the other degrees of freedom, so the resulting surfaces represent the free energy. Since it is difficult to plot surfaces in four-dimensional space, we discuss the situation for fixed values of the coordinate  $d_a$  of the adsorbed hydrogen atom. For convenience, we set the energy of the initial state, consisting of an adsorbed hydrogen atom and a proton in the solution, at SHE equal to zero. Since at SHE the first step of the hydrogen evolution is uphill at Ag(111), the Heyrovsky reaction is downhill.

So we have calculated free energy surfaces for various positions of  $H_a$  and determined the energy of activation for

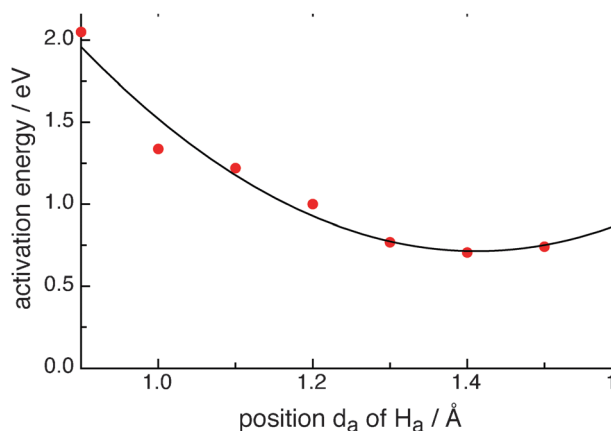


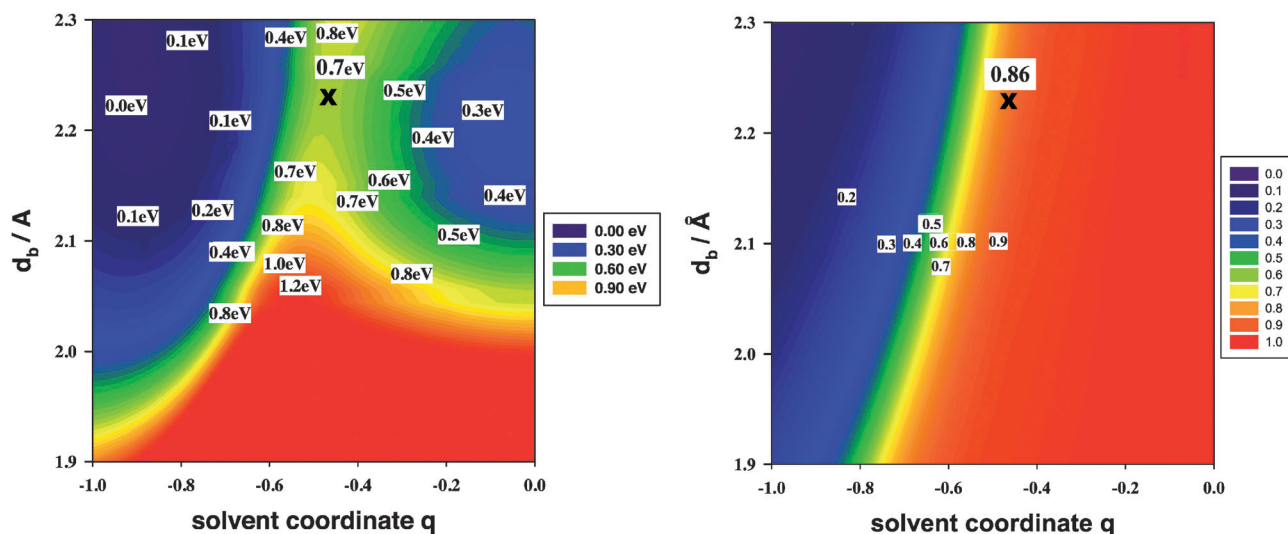
Fig. 7 Energy of activation at the equilibrium potential as a function of the position  $d_a$  of the adsorbed hydrogen atom.

the equilibrium potential SHE. The result is shown in Fig. 7 and reflects two opposing tendencies. As we had noted when we discussed Fig. 2, the hydrogen molecule is repelled from the surface; this raises the energy of the final state and is unfavorable. On the other hand, electron transfer to the approaching atom is favored at a short distance from the surface, and a movement of the adsorbed atom away from its equilibrium position also costs energy (see Fig. 1). Therefore, the energy of activation at first decreases with growing distance  $d_a$ , passes through a minimum, and then rises. The minimum is attained at  $d_a \approx 1.4$  Å with an activation energy of about 0.7 eV. Thus, it is of the same order of magnitude as for the first step in hydrogen evolution, hydrogen adsorption.<sup>12</sup> This is in line with experimental data, which indicate that on silver both reactions proceed roughly with the same speed.<sup>13,14</sup>

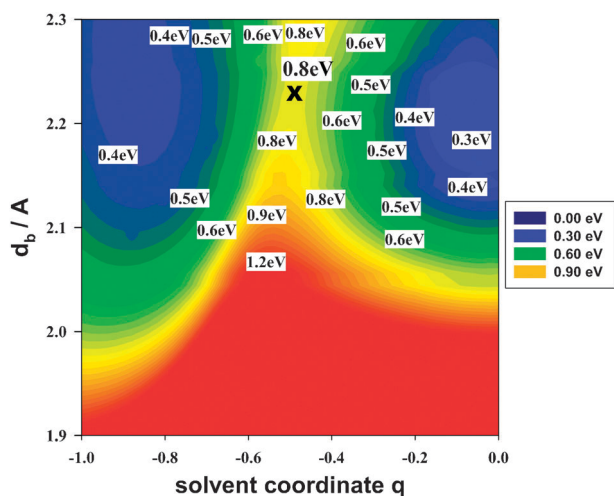
The corresponding free energy surface, plotted as a function of the position  $d_b$  of the second atom and the solvent coordinate  $q$ , reveals more details about the reaction (see Fig. 8). At the final state the second atom  $H_b$  is at a distance of about 0.8 Å from  $H_a$ , which corresponds to the binding distance of the free molecule. The saddle point for the reaction is at about the same distance, indicating that  $H_b$  first approaches to the binding distance before electron transfer takes place. In addition we note that at this configuration the reaction is still uphill, even though the total reaction is downhill. The newly-formed hydrogen molecule gains energy as it leaves the surface (see Fig. 2).

We have also investigated the effect of the reorganization energy  $\lambda$  on the height of the activation barrier. Varying  $\lambda$  in the range of 3–4 eV practically has no effect on the activation barrier. In a normal electron transfer reaction we would expect an increase of the activation barrier with  $\lambda$ . However, as noted before,<sup>12</sup> this effect is offset by the initial state energy given by eqn (11).

The occupancy of the 1s orbital of  $H_b$  changes from zero to unity during the reaction; the right hand side of Fig. 8 shows its value as a function of  $d_b$  and  $q$ . On the saddle point, it takes a value of about 0.86, and is thus close to that of the final state. In Marcus-type theories, this value should be close to that of the transfer coefficient,  $\alpha$ , which gives the change of the activation energy with the reaction free energy, which is given



**Fig. 8** Left: free energy surface for the case where the adsorbed atom  $H_a$  is at a distance of 1.4 Å. Right: corresponding occupancy of the 1s orbital of  $H_b$ ; the saddle point is indicated by a cross.



**Fig. 9** Free energy surface for the case where the adsorbed atom  $H_a$  is at a distance of 1.4 Å, and for an overpotential of  $\eta = -0.4$  eV.

by the overpotential. Varying the electrode potential is not a problem in our theory, so Fig. 9 shows the free energy surface for an overpotential  $\eta = -0.4$  eV. The energy of the initial state near  $q = -1$  and  $d_b = 2.4$  Å has been raised by 0.4 V (see eqn (11)), while the energy of the saddle point has been raised to about 0.8 eV. Thus, the energy of activation has been reduced to 0.4 eV. Varying the overpotential  $\eta$  in the region of  $\pm 0.4$  V, we obtain a value of  $\alpha \approx 0.75$  to  $-0.85$ , close to the occupation at the saddle point. This similarity with the Marcus theory is due to the fact that the reaction practically occurs at constant positions of the two atoms, so that the solvent coordinate is also the reaction coordinate, and it resembles a pure electron transfer. This also explains the comparatively high value of  $\alpha$ : in the Marcus theory,  $\alpha > 1/2$  when the reaction is uphill. We note in passing that it is an advantage of our theory over pure DFT that the electrode potential is well defined.

Thus, the Heyrovsky reaction proceeds in the following way: the proton approaches the surface, and at the same time

the adsorbed hydrogen atom detaches itself somewhat from the surface. When the two particles are at a distance of about 0.8 Å away from each other, which corresponds to the binding distance of the hydrogen molecule, a thermal fluctuation triggers an electron transfer to the proton, and the molecule then forms spontaneously. Qualitatively, these findings are in line with the early work of Dogonadze *et al.*,<sup>15</sup> in which electron transfer is assumed to be the rate-determining step. Their theory would also predict a transfer coefficient of  $\alpha > 1/2$  for an endergonic step.

Since the d band of silver lies well below the Fermi level, and its coupling with the approaching hydrogen is weak, it is pertinent to ask if it really plays a role in the Heyrovsky reaction. If we simply set the coupling constant  $V_b = 0$ , leaving everything else unchanged, the energy of activation rises by about 0.09 eV, *i.e.* a few  $kT$ , which is a comparatively small amount. However, on the real sp metal like cadmium or mercury the energy of the adsorbed hydrogen is higher by about 0.5 eV, which would raise the activation energy further. Thus we may conclude that the role of the d band in the electron transfer step itself is not so important.

## 5. Conclusion

Our work is the first theory for the Heyrovsky step in hydrogen evolution. Following the spirit of our previous work,<sup>12</sup> we have proposed a model Hamiltonian and combined it with DFT calculations. The latter served a dual purpose: with their aid we obtained the important system parameters, and we corrected the energies for correlation and exchange effects that are missing in our model. When the solvent coordinate takes the value of  $q = 0$  corresponding to an uncharged system, our energies reduce to the DFT results. Thus, in a certain sense our interpolation formula eqn (10) extrapolates the DFT results to the relevant range of solvent coordinates. Like in all theoretical work, the quality of our approximations is difficult to assess a priori. However, we have used very similar approximations in our theory for proton adsorption, and this has been quite

successful in explaining the catalytic activities both of pure and nanostructured metals, so we have reasons to be optimistic.

The alternative to a proper theory are pure DFT calculations for very large ensembles. This is the approach that has been taken in the only other works in which the Heyrovsky reaction has been considered from a microscopic point of view, that of Skulason *et al.*<sup>1,2</sup> As is inevitable in DFT, the authors start from an unrealistic model for the double layer, which is represented by several bilayers of water, a structure that is not stable at room temperature.<sup>28</sup> There is no thermal averaging, and the electrode potential is obtained by an extrapolation scheme assuming a constant double-layer capacitance. These authors considered this reaction on a Pt(111) electrode, so the results are difficult to compare, particularly since purely numerical calculations give fewer details and insights than theory. In ref. 1 this group obtained an activation energy of about 0.3 eV at SHE, while in ref. 2 it has risen to about 1 eV, showing the large uncertainty of this approach. However, another qualitative point is noteworthy: the authors of ref. 1 noted that the hydrogen atoms adsorbed in the threefold hollow sites do not react, but have to be moved to the on-top position. This corresponds to our findings that on Ag(111) the adsorbed hydrogen atoms have to move by about 0.5 Å away from their positions in order to react.

So far, we have performed model calculations only for Ag(111), on which the Heyrovsky reaction is known to be the dominant second step. The application to other metals should be straightforward. The general approach can be applied with minor modifications to other simple biatomic reactions like  $H_{ad} + OH^- \rightarrow H_2O + e^-$ , which is a step in the hydrogen reaction in alkaline solutions.

## Appendix

### Green's function

Green's function is a special case of the one that we derived in a recent publication for bond-breaking reactions with non-equivalent product atoms.<sup>18</sup> As mentioned in the Introduction, we may ignore spin polarization; also, only the approaching atom  $H_b$  interacts with the solvent. We give the matrix element for its orbital:

$$\langle b|G^+(\varepsilon)|b\rangle = \frac{\varepsilon - \varepsilon_a - \Lambda_a + i\Delta_a}{(\varepsilon - \varepsilon_b + 2\lambda q - \Lambda_b + i\Delta_b)(\varepsilon - \varepsilon_a - \Lambda_a + i\Delta_a) - \beta^2} \quad (12)$$

where  $\Delta$  and  $\Lambda$  contain contributions both from the interaction with the d band and the sp band. The corresponding Green's function element for the atom  $H_a$  is obtained by interchanging the indices a and b, and dropping the term in  $\lambda$ . The density of state is obtained from the usual relation:

$$\rho(\varepsilon) = -\frac{1}{\pi} \Im G^+(\varepsilon) \quad (13)$$

where  $\Im$  denotes the imaginary part.

### Technical details

All calculations were performed using the DACAPO code.<sup>29</sup> 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 ultra-soft pseudopotentials,<sup>30</sup> which allows 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 (GGA) in the version of Perdew, Burke and Ernzerhof.<sup>31</sup> The Brillouin zone integration was performed using a  $8 \times 8 \times 1$  k-point Monkhorst-Pack grid<sup>32</sup> corresponding to the  $(1 \times 1)$  surface unit cell. The surfaces were modeled by a  $(2 \times 2)$  supercell with four metal layers and 10 layers of vacuum. Dipole corrections were used to avoid slab–slab interactions.<sup>33</sup> The first two layers were allowed to relax, while the bottom two layers were fixed at the calculated nearest 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 system, we performed a series of calculations for a single hydrogen 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 1s orbital of hydrogen. The calculations for the hydrogen atoms were performed with spin polarization.

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