

# Recent Advances in Theoretical Aspects of Electrocatalysis

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## I. INTRODUCTION

Although electrochemistry has much in common with surface science, the application of the principles of catalytic activity to the reactions taking place in an electrochemical environment is not straightforward. All electrochemical reactions of practical interest imply at least one step where an electron is transferred between species coming from the solution side or the electrode surface. Therefore electrochemical reactions occurring at the interfaces are governed by the interaction of the reactant both with the solvent and with the electrode. There is also an additional effect produced by the external applied potential, so that the Fermi level of the reactant can be easily *tuned* relative to the Fermi level of the electrode.

Much research effort has been directed at understanding the mechanism of electrocatalysis. Various empirical attempts have been made to correlate the reaction rate with other quantities. Phe-

nomenological correlations were established between the reaction rate and various properties such as the work function,<sup>1</sup> the strength of the metal-hydrogen bond,<sup>2,3</sup> and the presence of empty d-orbitals.<sup>4</sup> One of these approaches was the application of Sabatier's principle,<sup>5</sup> which states that for a reaction to proceed rapidly the intermediates should have an intermediate energy of adsorption; a weak adsorption proceeds too slowly, a strong adsorption blocks the surface. On this basis, a volcano plot of the reaction rate versus the energy of adsorption was proposed by several authors<sup>1-4,6-8</sup> as indication of the electrocatalytic activity of different electrodes materials for the hydrogen oxidation. However, all the metals on the descending branch of such plots (Ti, Ta, Nb) are covered by an oxide film, which greatly reduces the rate, a fact that was not known when this relation was established. It is important to stress that this principle cannot be applied to the electrochemical hydrogen reaction in the same manner as for gas-phase surface reactions, since the free energy of adsorption of hydrogen from the solution varies with the electrode potential, and a metal that adsorbs hydrogen weakly at the equilibrium potential will adsorb strongly at more negative potentials. Taken to its logical conclusion, a simple application of Sabatier's principle would result in volcano-shaped current potential curves, which is absurd.<sup>9</sup> Another aspect that has been widely discussed is the role of the *d bands*. All good catalysts, such as platinum and palladium, possess *d bands*. However, on other *d* metals such as nickel and cobalt the reaction proceeds quite slowly, and so the mere presence of a *d band* is not sufficient to assure good catalytic properties. A more quantitative treatment based on a model taking into account all contributions of the different components of an electrochemical system and the corresponding interactions must be considered.

In a homogenous phase the determining factor for electron transfer between charged species is the reorganization of the solvent. This process is well understood within the Marcus and Hush theory.<sup>10,11</sup> On the other hand, recent developments in theoretical approaches of surface science, especially those based on density functional theory (DFT),<sup>12-14</sup> have contributed to a better understanding of surface processes and the effects of electronic interactions between reactants and catalysts. In this context, the relative energies of the electronic levels of the reactants and the catalyst and the corresponding coupling strengths play the key role. In order to

describe the *reaction path* (initial, transition and final states), different coordinates can be considered to represent the potential energy. In the case of reactions in the gas phase, the distance to the catalyst and the separation between the atoms taking part in reactions involving bonds breaking are usually employed. In electrochemical systems an additional coordinate, the *normalized solvent coordinate*, must also be considered. Realistic calculations must take into account all the diverse important contributions mentioned above.

In our group we have developed a new approach for electrochemical system, using DFT calculations as input in the SKS Hamiltonian developed by Santos, Koper and Schmickler.<sup>15,16</sup> In the framework of this model electronic interactions with the electrode and with the solvent can be included in a natural way. Before giving the details of this theory, we review the different phenomena involved in electrochemical reactions in order to understand the mechanism of electrocatalysis and the differences with catalysis in surface science. Next, a brief summary of previous models will be given, and finally the SKS Hamiltonian model will be discussed. We will show how the different particular approaches can be obtained on the basis of the generalized model. As a first step, idealized semielliptical bands shapes will be considered in order to understand the effect of different parameters on the electrocatalytic properties. Then, real systems will be characterized by means of DFT (Density Functional Theory). These calculations will be inserted as *input* in the SKS Hamiltonian. Applications to cases of practical interest will be examined including the effect not only of the nature of the material but also structural aspects, especially the electrocatalysis with different nanostructures.

## II. CLASSIFICATION OF ELECTROCHEMICAL REACTIONS

When a reactive species approaches the electrode surface besides its interaction with the solvent also electronic interactions with the electrode come into play (see Figs. 1 and 2). Depending on their relative intensities the electrochemical reaction can proceed through two different mechanisms. If the interaction with the electrode is comparatively weak, the reactant preserves its whole sol-

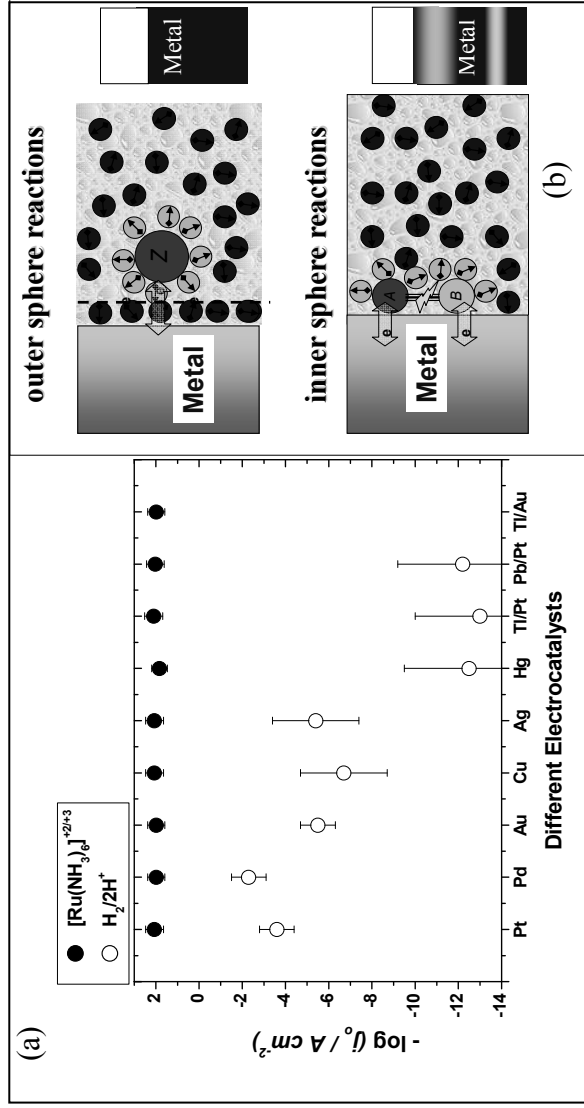


Figure 1. (a) experimental values of the standard exchange current for an outer sphere reaction (filled symbols); data obtained from Refs. 17 and 18 and for an inner sphere reaction, such as the hydrogen oxidation reaction; data obtained from Ref. 3 and 4. (b) schematic representations of outer and inner sphere reactions.

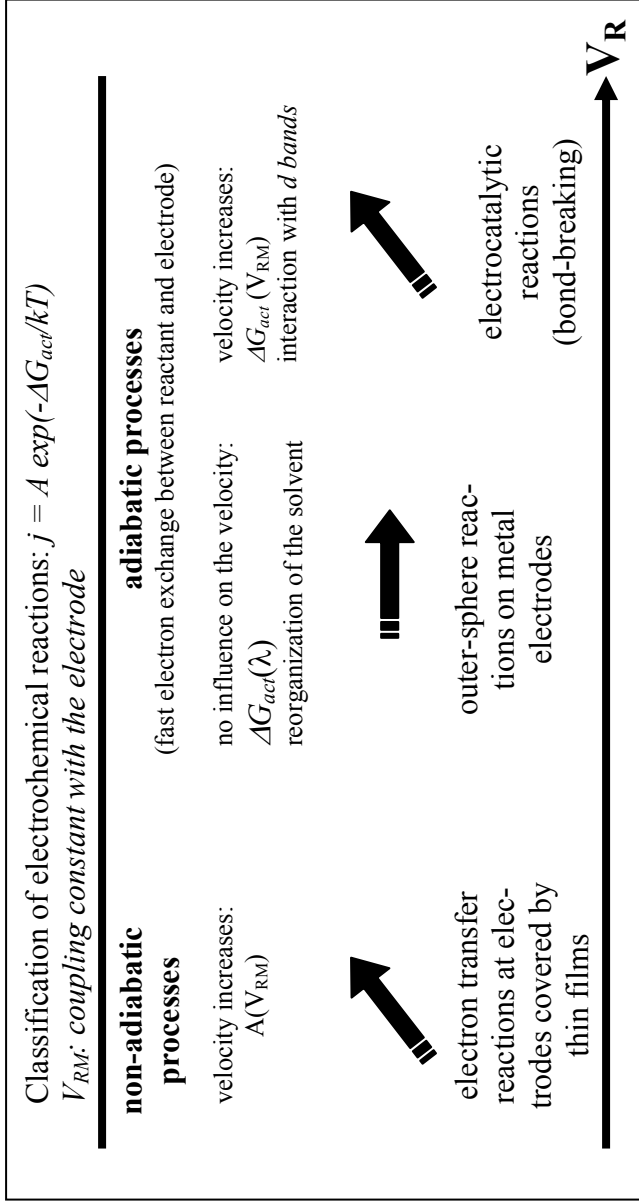


Figure 2. Classification of electrochemical reactions according to the strength of the interaction with the electrode.

vation shell. This is an *outer sphere electron transfer reaction*; the reactant is not in direct contact with the electrode surface. At least one layer of solvent or some other ligand separates reactant and electrode. Although the reactant preserves its inner shell, the solvent in the vicinity of the reactant must reorient during the reaction because reactant and product carry different charges. The reaction rate is mainly determined by this reorganization of the solvation shell and the theoretical basis is given by the extension of Marcus – Hush model.<sup>10,11</sup> In this case the nature of the metal does not play any important role; there is no catalysis, since the electrode behaves simply as an electron reservoir. These types of reactions are usually very fast since electrons can tunnel when the solvation sheath has acquired a suitable configuration. During the reaction no bonds are broken or formed, and no specific adsorption takes place. Typically such reactions occur *adiabatically* at bare metal electrodes and involve metal ions surrounded by inert ligands. The interactions between the reactant and the metal by *adiabatic* reactions are sufficiently strong such that the electron exchange takes place every time the system reaches the transition state. Thus the system is in electronic equilibrium for all solvent configurations. Because of the high velocities, there are experimental difficulties to determine the rate constants for these reactions, and fast transient methods or techniques forcing convection for the mass transport are required.<sup>17,18</sup> Then, if appropriate measurements are performed, no appreciable dependence on the nature of the metal is observed, as it is shown in Fig. 1 for the redox reaction  $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ . In the case that the electronic interactions are weaker, the system can pass the saddle point of the reaction coordinate without an electron transfer, so that it subsequently returns to its initial state. These reactions are called *non-adiabatic*, and the interaction strength will enter into the pre-exponential factor of the expression for the velocity. They can be modelled by the perturbation theory through the Levich – Dogonadze approach.<sup>19</sup> Examples of such reactions are electron transfers through thin films and we will not discuss them in this work.

When reactions involve bonds rearrangement, or adsorption, the reacting species loses a part of its solvation shell and moves close to the electrode surface. They are called *inner sphere electron transfer reactions* and the electronic interactions with the electrode can be either weak or strong. Depending on the elec-

tronic structure of the electrode the reaction can be catalyzed or not. Two important electrochemical reactions which require catalysis are the hydrogen oxidation – evolution and the oxygen reduction – evolution reactions. The standard exchange current obtained for the first reaction with different electrode materials is also shown in Fig. 1. The reaction rate is much slower (about at least four order of magnitude lower) than the outer sphere reactions and a strong dependence on the nature of the metal is observed (about eight order of magnitude between the best and the worst electrocatalyst!!)

In the literature there are several theoretical approaches that describe the different particular processes. The model we have proposed can explain all the different cases and takes into account all the possible interactions.

### III. PREVIOUS APPROACHES TO CATALYSIS FROM THE SURFACE SCIENCE

There are in the literature several reviews about this topic (see for example Refs. 20-22). In this Section we discuss only the more relevant aspects related to the concepts that can be applied to electrochemical systems.

The electronic of the catalyst determines its activity. In solid materials the electronic levels form bands of allowed energies separated by band gaps. At  $T = 0$  the bands are filled up to a certain level, the Fermi level  $\varepsilon_F$ . It is a characteristic of metals that the Fermi level lies inside an energy band, which is therefore only partially filled. At finite temperatures, electrons can be excited thermally to higher levels. However, at room temperature the thermal energy is about 0.025 eV; often energies of this order of magnitude are negligible, and the Fermi-Dirac distribution can then be replaced by a step function. Usually the bands are labelled by the single orbitals of which they are composed. Thus, we can speak of a *1s* or a *3d band*. The bands are the wider, the greater the overlap between the orbitals. *sp* bands, which are composed of the *s* and *p* orbitals form rather large structureless bands. In contrast, *d* orbitals are more localized and form narrow *d bands*. Figure 3 shows schematically the band structure of a few typical electrode materials: A semiconductor or insulator, which could be also a

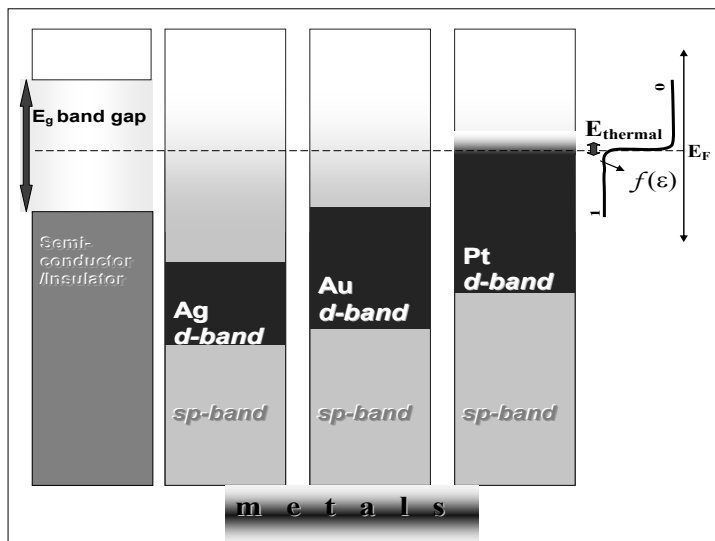


Figure 3. Schematic representation of the electronic bands structure of different types of materials. The Fermi-Dirac distribution determines the occupation of the electronic states.

metal electrode covered by an oxide film, and three different metals. All three metals possess a wide *sp band* extending well above the Fermi level. However, the *d bands* are different. The position of the *d band* of silver is lower than that of gold, and both lie lower than that of platinum. In the latter case the *d band* even extends about 0.5 eV above the Fermi level. These differences are crucial for determining the electrocatalytical properties of these materials. Hammer and Nørskov<sup>23</sup> have proposed a simple one-electron description of the quantum mechanics of atoms and molecules interacting with all valence states of the metal surfaces (see Fig. 4). This interaction is formally composed of a contribution (*weak chemisorption*) arising from the *sp bands* which leads to a broadening and a shift of the atomic level to lower energies (*renormalization*) and a second contribution (*strong chemisorption*) coming from the *d bands*. The latter involves a strong *hybridization* which produces a split in a bonding and an antibonding contribution just as in a simple two-state problem, where the whole *d band* is re-

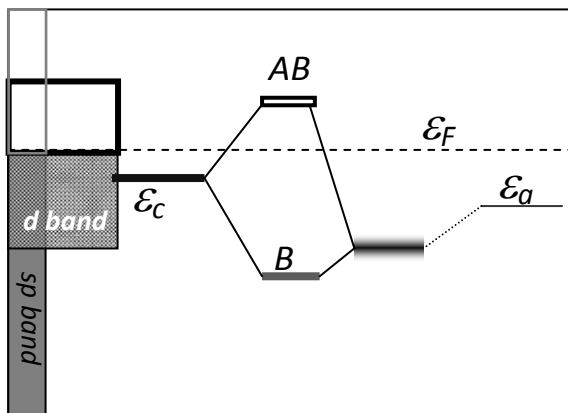


Figure 4. Simple model regarding the whole *d band* as a single level located at its center and interacting with an adsorbate.

placed by an effective level located at its center. A similar concept has been previously developed for gas phase reactions,<sup>24</sup> where the substrate *frontier orbitals* simultaneously play the role of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital). This model provides a qualitative picture for the catalytic effect of the *d bands*. The higher the position of the center of the *d band*, the smaller is the occupation of the antibonding orbital and the more attractive results the interaction. They proposed a linear relationship between the *d band* center position shift  $\delta\epsilon_c$  and the change in the chemisorption adsorption contribution  $\delta E_{ads}$ :

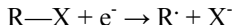
$$\delta E_{ads} = -\frac{V^2}{\epsilon_c^d - \epsilon_a} \delta\epsilon_c^d \quad (1)$$

In the case of coin metals like Au and Ag (see Fig. 3), the center of the *d band* lies too low and thus both bonding and antibonding levels are situated below the Fermi level and in consequence are filled making the interaction repulsive. The opposite happens with Pt, which is a good catalyst. In this case, the center of the band is situated near the Fermi level, and thus the bonding

level appears below the Fermi level, while the antibonding lies above it. This intuitive approach is simple and provides a good tool to estimate the catalytic properties of different materials according to their electronic structures, particularly for comparing similar systems that only differ in the position of the *d band* center. However, in order to understand *electrocatalysis* in an electrochemical environment a more extensive framework is necessary. As we will see below, the position of the electronic level of the reactant can be shifted by fluctuations of the solvent configuration and by changing the applied potential. These effects make the analysis more complicated.

#### IV. PREVIOUS APPROACHES TO BOND BREAKING ELECTROCHEMICAL REACTIONS

The first approaches towards a theory for electrochemical reactions in which bonds are broken were given independently by German and Kuznetsov<sup>25</sup> and Savéant<sup>26,27</sup> for reactions such as:



A simple model based on a Morse curve description of the potential energy surface for bond-breaking (see Fig. 5) has been proposed:

$$V(R) = D_e \left( e^{-2\alpha R} - e^{-\alpha R} \right) \quad (2a)$$

$$V(R) = D_e e^{-2\alpha R} \quad (2b)$$

The first equation represents the situation before, while the second one describes the behaviour after the bond breaking.  $D_e$  is the dissociation energy of the *RX* bond. This leads to a quadratic activation driving force free energy relationship:

$$\Delta G_{act} = \frac{(\lambda + D_e - e_o \eta)^2}{4(\lambda + D_e)} \quad (3)$$

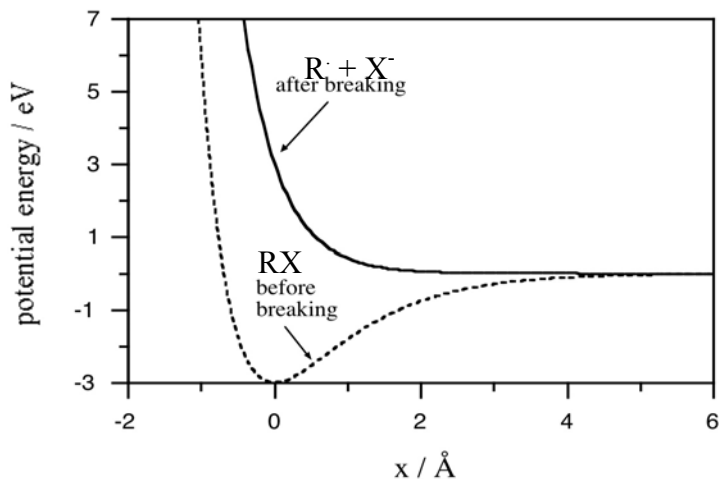


Figure 5. Simple model based on a Morse curve description of the non-adiabatic potential energy surface for bond-breaking.

If the system is under equilibrium conditions, the overpotential  $\eta$  is zero and the standard activation free energy becomes the sum of two contributions characterizing bond-breaking ( $D_e$ ) and solvent reorganization ( $\lambda$ ), respectively:

$$\Delta G_o^\# = \frac{D_e + \lambda}{4} \quad (4)$$

A further development of this theory has been carried out by Koper and Voth<sup>28,29</sup> considering the electronic coupling with the electrode which was absent in Savéant's model for calculating adiabatic potential energy surfaces:

$$\hat{H}_{tot} = \hat{H}_{electrode} + \hat{H}_{solvent} + \hat{H}_{aa} \quad (5)$$

As in Savéant's model they describe the R—X bond by a Morse potential and introduce an effective switching operator describing the bond breaking process:

$$\hat{H}_{aa} = D_e [1 - n_{AB}] \{1 - \exp[-\gamma(r - r_o)]\}^2 + D_e n_{AB} \exp[-2\gamma(r - r_o)] \quad (6)$$

where  $D_e$  is the dissociation energy of R—X,  $n_{AB}$  the occupation number operator of the antibonding orbital ( $AB$ ),  $\gamma$  is related to the bond vibration frequency,  $r$  is the bond distance and  $r_o$  the equilibrium bond distance.

The Koper–Voth model does not account for spin, and refers therefore to the exchange of one electron with a comparatively weak interaction. Kuznetsov et al. have introduced the spin interaction for bond breaking reactions<sup>30</sup> in the usual Hartree–Fock approximation.<sup>31,32</sup> In the limit of an infinitely wide, structureless metal conduction band, Kuznetsov and Medvedev<sup>33</sup> have shown how to go beyond the Hartree–Fock approximation by using a solution of the Anderson Hamiltonian<sup>34</sup> by Kawakami and Akiji,<sup>35</sup> which is exact in this limit. They have also applied their model to bond-breaking electron transfer induced by a scanning tunneling microscope.<sup>36</sup> An important limitation of all these contributions is that the potential energy curves for the intact molecule and for the two fragments were introduced in an ad hoc manner. This can either be done by the explicit introduction of an operator<sup>28,29</sup> which switches between the states before and after bond breaking, or, equivalently, by introducing different potential energy curves in the presence and in the absence of the valence electrons.<sup>30</sup> In order to understand the electrocatalysis process for strong interaction with the electrode important changes in these models are necessary.

## V. MODEL HAMILTONIAN

A general model Hamiltonian for electron transfer in an electrochemical environment<sup>15,16</sup> must contain terms for the different components of the system, i.e., the reactant, the electrode and the solvent, and their corresponding interactions:

$$\hat{H}_{tot} = \hat{H}_{electrode} + \hat{H}_{reactant} + \hat{H}_{solvent} \quad (7)$$

It is more convenient to express the different contributions in second quantized form. Thus, we have for the electrode and its interaction with the reactant:

$$\hat{H}_{electrode} = \sum_{k,\sigma} \varepsilon_k n_{k,\sigma} + \sum_{k,a,\sigma} [V_{ak} c_{k,\sigma}^\dagger c_{a,\sigma} + V_{ak}^* c_{a,\sigma}^\dagger c_{k,\sigma}] \quad (8)$$

$k$  labels the electronic states in the electrode,  $n_k$  are the corresponding number operators, and the last term effects electron exchange between the electrode and the different orbitals of the reactant labelled as  $a$ .  $c^\dagger$  and  $c$  denote the creation and annihilation operators respectively.  $\sigma$  is the spin index. The contributions of interactions between the solvent and the electrode itself are usually not important for the electrochemical rate,<sup>37</sup> however they can be included if necessary.

In order to describe the state of the solvent, we represent it as a bath of harmonic oscillators, which interact linearly with the reactant. The corresponding Hamiltonian is written in the form:

$$\hat{H}_{solvent} = \frac{1}{2} \sum_{\nu} \hbar \omega_{\nu} (\tilde{p}_{\nu}^2 + \tilde{q}_{\nu}^2) + \sum_{a,\sigma} (Z_a - n_{a,\sigma}) \sum_{\nu} \hbar \omega_{\nu} g_{\nu} \tilde{q}_{\nu} \quad (9)$$

Here  $Z_a$  is the charge number of the reactant  $a$ ,  $\nu$  labels the phonon modes, which have frequencies  $\omega_{\nu}$ , dimensionless coordinates  $\tilde{q}_{\nu}$  and momenta  $\tilde{p}_{\nu}$ , and  $g_{\nu}$  is the interaction constant of the reactant charge with the mode  $\nu$ . For a classical solvent the multi-dimensional representation given in Eq. (9) can be replaced by an equivalent one-dimensional model. Then the interaction between the solvent and the reactant can be characterized by a single energy of reorganization defined as:

$$\lambda = \sum_{\nu} \frac{1}{2} \hbar \omega_{\nu} g_{\nu}^2 \quad (10)$$

Here the generalized coordinate  $q = \tilde{q}g$  has been normalized and has the following meaning: When the reactant having a charge  $-q$  is in equilibrium with a given configuration of the solvent, the sol-

vent state is characterized by the value of  $+q$ . Thus we can rewrite Eq. (9) in the following way:

$$\hat{H}_{solvent} = \lambda \left[ p^2 + q^2 + 2 \sum_{a,\sigma} (Z_a - n_{a,\sigma}) q \right] \quad (11)$$

The contribution of the reactant, consisting in the general case of a molecule composed of different atoms, can be expressed in the following generalized form<sup>15,16</sup>:

$$\hat{H}_{react} = \sum_{a,\sigma} \left[ \varepsilon_a n_{a,\sigma} + \sum_{a'} \left( \beta_{aa'} c_{a\sigma}^+ c_{a'\sigma} + \beta_{aa'}^* c_{a'\sigma}^+ c_{a\sigma} + V_{imag}^{aa'} \right) + U_a n_{a\sigma} n_{a\sigma} \right] \quad (12)$$

Here  $a$  is the index for the different valence orbitals of the reactant participating in the reaction;  $n$  is a number operator which account for the occupation of the given state, the terms involving creation and annihilation operators effect electron exchange and are responsible for the bonding between two orbitals in the reactant and is related to the bonding energy. During the reaction of electron transfer the atoms of the molecule become charged due to the electron transfer process with the electrode. Charged species near a metal surface induce an image charge on the metal and interactions between the *core* of the reactant and the electrode surface take place (see Fig. 6). Then we have to add a term  $V_{imag}$  to the Hamiltonian, which is approximated as a dipole-dipole interaction term:

$$V_{imag}^{aa'} = \alpha_{dip} \left[ Z_a - \sum_{\sigma} n_{a,\sigma} \right] \left[ Z_{a'} - \sum_{\sigma} n_{a',\sigma} \right] \quad (13)$$

where:

$$\alpha_{dip} = \frac{4(d_{Elec})^2}{(r + 2r_o)^3} \quad (14)$$

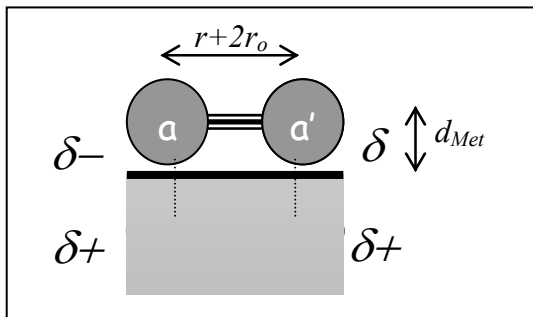


Figure 6. Dipole-dipole interaction produced as a consequence of the induced image charge on the metal by the partially charged species during the bond breaking, according to Ref. 16.

$Z_a$  and  $Z_{a'}$  are the charge numbers of the atoms  $a$  and  $a'$  respectively when the atomic orbital  $a(a')$  is empty;  $d_{Elec}$  is the distance of the atoms to the electrode surface,  $r$  is the distance between the atoms and  $r_o$  is the equilibrium distance between the atoms. The last term containing  $U$  stands for the Coulomb repulsion between the electrons of opposite spin in the same orbital.

The total Hamiltonian can be solved by Green's function techniques<sup>38</sup> using the Hartree-Fock approximation for the Coulomb repulsion terms:<sup>32,33</sup>

$$Un_i n_j \approx Un_i \langle n_j \rangle + Un_j \langle n_i \rangle - U \langle n_i \rangle \langle n_j \rangle \quad (15)$$

where  $\langle \dots \rangle$  denotes the expectation value.

In particular the density of states of the different orbitals and their corresponding occupation numbers, and the energy can be calculated.

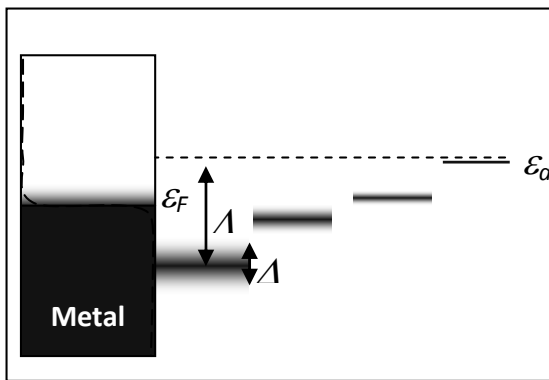


Figure 7. Broadening and shift of the electronic level of an adsorbate approaching to the surface of a metal.

## VI. INTERACTIONS OF THE ATOMIC ORBITALS OF THE REACTANT WITH THE ELECTRONIC STATES OF THE ELECTRODE

These phenomena are well described by Anderson-Newns Model<sup>34,39</sup>. Two main effects occur when an atomic orbital of the reactant interacts with the electronic levels of the electrode. When the reactant approaches the surface, the energy level of the orbital interacts with all electronic states on the electrode characterized by the electronic energy  $\varepsilon$ . It shifts with respect to the position of the isolated species  $\varepsilon_a$ , and simultaneously there is a *broadening* (see Fig. 7). It is no longer characterized by a sharp level, but by a density of states  $\rho_a(\varepsilon)$ . The binding of the reactant to the surface depends on the quantum-mechanical coupling of the reactant and on the electrode wave functions. These two effects are described through the *chemisorption functions*  $\Delta$  (broadening) and  $\Lambda$  (shift) which are interrelated through a Hilbert transform:<sup>34,39</sup>

$$\Delta(\varepsilon) = \pi \sum_k |V_{ak}|^2 \delta(\varepsilon - \varepsilon_k) ; \quad \Lambda(\varepsilon) = \frac{P}{\pi} \int \frac{\Delta(\varepsilon')}{\varepsilon - \varepsilon'} d\varepsilon' \quad (16)$$

where  $P$  denotes the Cauchy principal value.  $\Delta(\varepsilon)$  is seen to be a weighted density of states functions corresponding to the electrode, with  $\Lambda(\varepsilon)$  as its Hilbert transform. The parameter  $\Delta$  has a simple interpretation: an electron placed on the reactant decays with a lifetime of  $\tau = \hbar/\Delta$  into empty states on the electrode; therefore  $\Delta$  can be thought of as a lifetime broadening, a manifestation of the Heisenberg uncertainty principle. Then, the projected density of states for the atomic orbital corresponding to the reactant is obtained from the imaginary part of the matrix elements of the Green functions and can be expressed through the following general form:

$$\rho_a(\varepsilon) = \frac{1}{\pi} \frac{\Delta(\varepsilon)}{[\varepsilon - \tilde{\varepsilon}_a - \Lambda(\varepsilon)]^2 + \Delta(\varepsilon)^2} \quad (17)$$

$\tilde{\varepsilon}_a$  is the position of the valence orbital at the surface and is affected not only by the interaction with the electrode but also with the electrochemical environment (see below, Section V). It contains also all exchange and correlations terms such as spin and image charges interactions missing in  $\Lambda(\varepsilon)$ . The shape of  $\rho_a(\varepsilon)$  is determined by the strength of the interactions with the electrode  $\Delta(\varepsilon)$ , which contains the coupling constants  $V_{ak}$  and the electronic structure given by the density of states  $\rho_{el}(\varepsilon)$ .

The simplest electrochemical reaction is an *outer sphere* electron transfer where the interactions with the electrode are weak. Hence, the details of the band structure are not important; we can ignore the  $k$  dependence of the coupling constants and replace them by a single effective value. The sum over  $k$  in Eq. (16) then reduces to the surface density of states corresponding to the electrode and the chemisorption function  $\Delta(\varepsilon)$  can be taken as constant. It corresponds to the interaction with a wide, structureless band on the electrode. In this approximation<sup>40-42</sup> the chemisorption  $\Lambda(\varepsilon)$  functions vanishes (see Fig. 8a):

$$\Delta(\varepsilon) = |V_{eff}|^2 \rho_{el}(\varepsilon) = \text{const}; \quad \Lambda(\varepsilon) = 0 \quad (18)$$

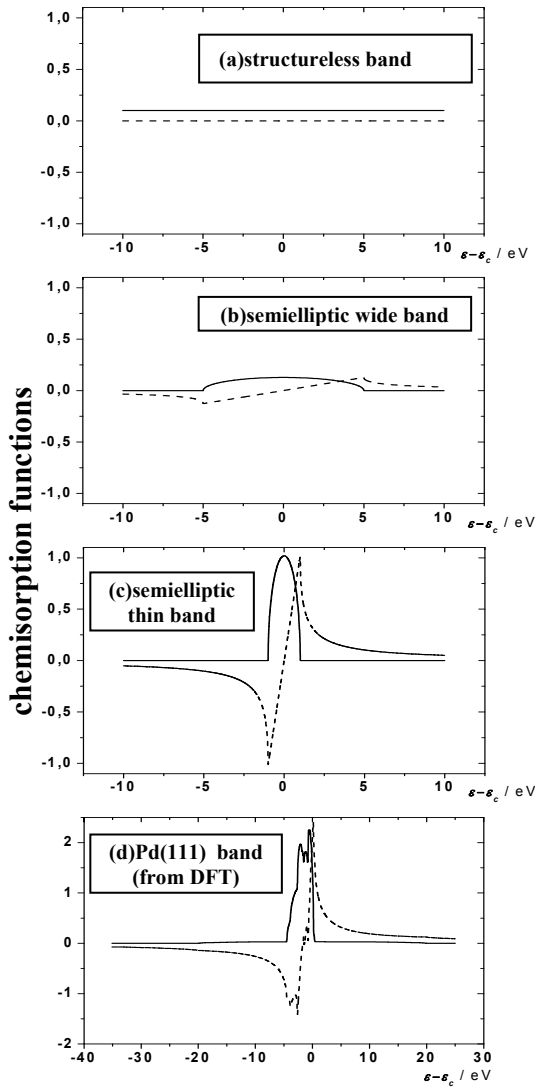


Figure 8. Different approaches to describe the electronic structure of the metal through the chemisorption functions  $\Delta(\varepsilon)$  (full lines) and  $\Lambda(\varepsilon)$  (dotted lines).

In this case the density of states of the reactant takes the form of a Lorentzian as illustrated in Fig. 9a.

In order to analyze the effects of the electronic structure on electrochemical reactions, it is useful to regard first idealized band shapes.<sup>43-45</sup> For this purpose we consider semi-elliptical bands as proposed by Newns,<sup>39</sup> where the density of states can be expressed by:

$$\rho_{el}(\varepsilon) = \left[ 1 - \left( \frac{\varepsilon - \varepsilon_c}{w} \right)^2 \right]^{1/2} \theta \left[ w^2 - (\varepsilon - \varepsilon_c)^2 \right] \quad (19)$$

Here the Heaviside function  $\theta$  ensures that the contribution vanishes outside the bands.  $\varepsilon_c$  and  $w$  indicate the center and the half width of the band, respectively. We still neglect any dependence of the coupling constants on  $k$  and consider an effective value, which is a good approximation for most cases. Then  $\Delta(\varepsilon)$  is proportional to  $\rho_{el}(\varepsilon)$  but no more constant;  $\Lambda(\varepsilon)$  can be easily obtained from equation (16). The effect on the density of states of the reactant  $\rho_a(\varepsilon)$  depends on the relative values of the parameters  $|V_{eff}|^2$ ,  $\tilde{\varepsilon}_a$ ,  $\varepsilon_c$  and  $w$ . In Fig. 8b and 8c we show the chemisorption functions for two semielliptic bands with different width, a wide band (Fig. 8b), which can represent a *sp band*, and a thinner one (Fig. 8c), which can describe a *d band*.

Figure 9 shows the resulting densities of states of the reactant. Here, the position of  $\tilde{\varepsilon}_a$  was selected such that it coincides with the center of the band  $\varepsilon_c$ . The results for  $\rho_a(\varepsilon)$  using a wide band (Fig. 9b) do not differ so much from the approximation with a constant  $\Delta$  (compare with Fig. 9a). However, when a thin band is present the interaction produces a broadening of the orbital of the reactant and in the case that the coupling is strong enough the orbital splits into bonding and anti-bonding parts with respect to the electrode (see the sharp peaks at both sides of the band in Fig. 9c). A model employing several semielliptic shapes to represent *d band* of real systems is very good, as can be appreciated from Fig. 8d, where a *real* electronic structure calculated for Pd(111) surface with DFT is shown. The shape of the corresponding  $\rho_a(\varepsilon)$  is very similar to that of Fig. 9c as can be inferred from Fig. 9d.

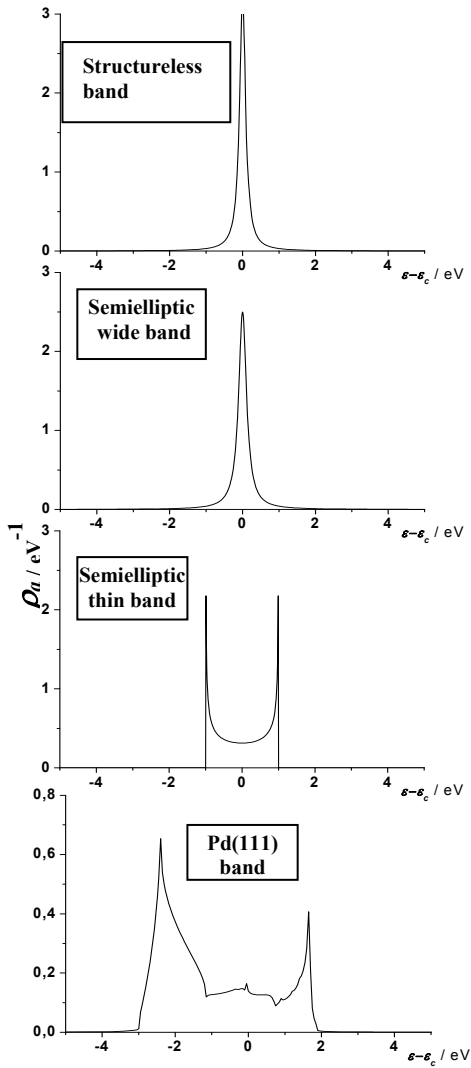


Figure 9. Density of states of the adsorbate  $a$  corresponding to the electronic structures of the metal given in Fig. 8

## VII. OCCUPATION PROBABILITY OF THE ELECTRONIC STATE OF THE REACTANT

The position of the electronic state of the reactant in the energy scale depends on a series of parameters, and in the following we will analyse them. Its occupation probability indicates if the electron transfer from (into) the electrode has occurred and to which extent. In the course of solvent fluctuations they may get energetically closer to the Fermi level or further away, and their density of states (DOS) changes accordingly.

As a first example we consider outer sphere reactions with weak interactions with the electrode. In this case only one electron is transferred and thus we consider only one electronic state for the reactant.<sup>40</sup> The first effect to be considered is the solvation. The reactant's levels fluctuate with the solvent. Its position depends on the solvent configuration and the center is given through:

$$\tilde{\varepsilon}_a = \varepsilon_a - 2\lambda q \quad (20)$$

The other interactions terms considered in the Hamiltonian of Eq. (12), such as spin and bonding between atoms, do not play any role in this case. In the course of the electron transfer the reactant changes its charge and hence its solvation; this situation is illustrated in Fig. 10. In the adiabatic case the reactant shares its electron with the metal. We have referred the electronic energy to the Fermi level of the electrode, which is taken as zero for convenience. Thus, the occupation of the electronic state of the reactant is obtained by integrating the density of states up to this energy value (see Fig. 11). Since Delta is constant in this simple case, an analytical expression can be obtained:<sup>40</sup>

$$\langle n_a \rangle = \int_{-\infty}^{\varepsilon_F=0} \rho_a(\varepsilon) d\varepsilon = \frac{1}{\pi} \arccot \cot \frac{\tilde{\varepsilon}_a}{\Delta} \quad (21)$$

The reactant can be neutral or a charged species. If an oxidation reaction takes place the electronic state lies well below the Fermi level and is completely occupied at the beginning of the reaction ( $\langle n_a \rangle = 1$ ); on the other hand, for a reduction reaction it

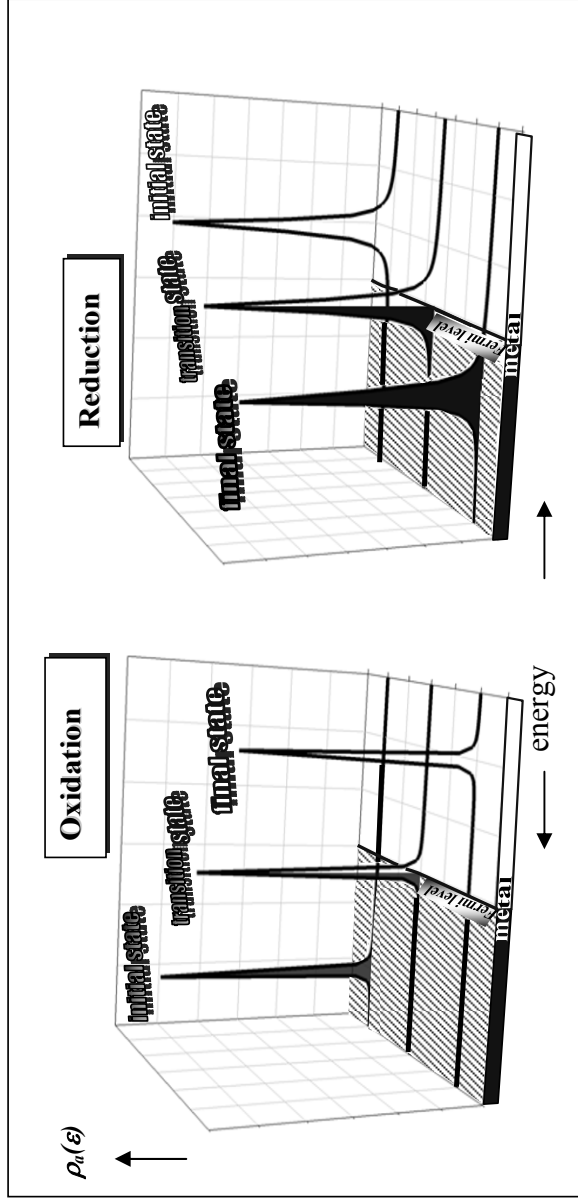


Figure 10. Evolution of the density of states of an adsorbate in the absence of a *d band* for an oxidation reaction (left) and a reduction reaction (right).

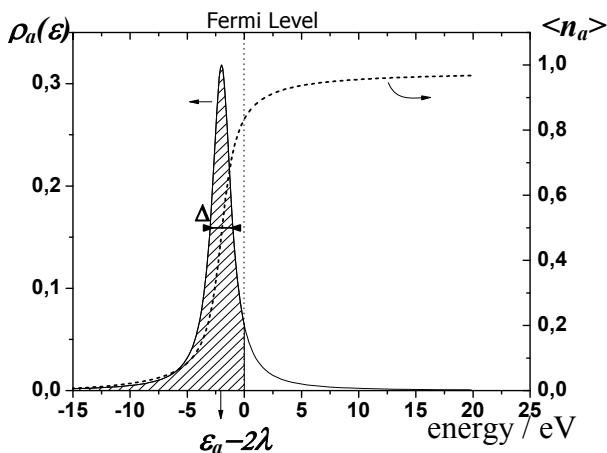


Figure 11. Density of states of the adsorbate  $a$  and the corresponding occupation obtained by integration according to Eq. (21).

is completely empty and is above  $\varepsilon_F$ . The configuration of the solvation shell determines the value of the normalized solvent coordinate and is opposite to its charge as mentioned in Section III. During the reaction an electron is transferred from (reduction) or into (oxidation) the electrode. There is a rearrangement of the solvent configuration; as a consequence the position of the center of  $\rho_a(\varepsilon)$  shifts and the occupation of the reactant orbital changes. At the transition state the electronic level of the reactant is about half occupied and at the final state it is totally empty (oxidation) or fully occupied (reduction). The solvent is relaxed to its new equilibrium position for the product. Table 1 summarizes the different possibilities according to the type of reaction and the initial charge of the reactant. Also the values of the normalized coordinate  $q$  are given for the different cases.

It is a great advantage of electrochemical system that the other parameter that produces a shift in the density of states of the reactant is the potential applied externally to the interface. The driving force of interfacial reactions can be varied with the elec-

**Table 1**  
**Different Types of Reactions and the Values of the Different Parameters**  
**(Normalized Solvent Coordinate and Occupation) for the Initial, the Tran-**  
**sition and the Final States of the Reactant.**

| reaction                                                                | initial state                                                                                                                   | transition state                                                                                                                                       | final state                                                                                                                                             |
|-------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------|
| $A \rightarrow A^+ + e$<br>$(H \rightarrow H^+ + e)$                    | AO  $q=0$<br>$\langle n \rangle = 1$          | AO  $q^{\ddagger} \sim 0.5$<br>$\langle n \rangle \sim 0.5$           | AO  $q=-1$<br>$\langle n \rangle = 0$                                  |
| $A \cdot \rightarrow A + e$<br>$(I \cdot \rightarrow I + e)$            | AO  $q=1$<br>$\langle n \rangle = 1$          | AO  $q^{\ddagger} \sim 0.5$<br>$\langle n \rangle \sim 0.5$           | AO  $q=0$<br>$\langle n \rangle = 0$                                   |
| $A^{x+} \rightarrow A^{x+1} + e$<br>$(Fe^{2+} \rightarrow Fe^{3+} + e)$ | AO  $q=x$<br>$\langle n \rangle = 1$          | AO  $q^{\ddagger} = (x+1)/2$<br>$\langle n \rangle \sim 0.5$          | AO  $q = -(x+1)$<br>$\langle n \rangle = 0$                            |
| $A_2 \rightarrow 2A^+ + 2e$<br>$(H_2 \rightarrow 2H^+ + 2e)$            | MO  $q=0$<br>$\langle n \rangle = 2$<br>$I_0$ | MO  $q^{\ddagger} \sim 1$<br>$\langle n \rangle \sim 1$<br>$I_{tran}$ | MO  $q=-2$<br>$\langle n \rangle = 0$<br>$I \rightarrow \infty$        |
| $A_2 + 2e \rightarrow 2A \cdot$<br>$(Cl_2 + 2e \rightarrow 2Cl \cdot)$  | MO  $q=0$<br>$\langle n \rangle = 2$<br>$I_0$ | MO  $q^{\ddagger} \sim 1$<br>$\langle n \rangle \sim 3$<br>$I_{tran}$ | MO  $q \sim 2$<br>$\langle n \rangle \sim 4$<br>$I \rightarrow \infty$ |

trode potential producing changes of the order of electron volts in the position of the electronic state participating in the reaction. Thus we can express  $\varepsilon_a$  for an oxidation (reduction) reaction as:<sup>40</sup>

$$\varepsilon_a = \varepsilon_a^{red/ox} + e_o \eta^{red/ox} \quad (22)$$

where  $\varepsilon_a^{red/ox}$  is its position when the species  $a$  is in thermodynamic equilibrium with the corresponding oxidized (reduced) product;  $\eta^{red/ox}$  is the related overpotential.

When the reactant is a molecule, we have to consider other terms coming from the interaction between the atoms forming the molecule. An interesting approach to understand the mechanisms of electron transfer in these cases is to describe the interaction of the molecule in terms of a tight-binding (or extended Hückel) model.<sup>15,16</sup> We consider here a particular case of a homonuclear molecule ( $A - A$ ) lying flat at the surface of the electrode; the molecule undergoes a simultaneous electron exchange with the electrode and the breaking of a single bond. Examples are the reduction of chlorine and the oxidation of hydrogen. However, an extension to more complicated cases, such as heteronuclear molecules ( $A - B$ ) or the exchange of more electrons in molecules with multiple bonds (for example oxygen) is possible. The important electronic states on the molecule are the bonding ( $B$ ) and antibonding ( $AB$ ) molecular orbitals which result from the interaction of the valence atomic orbitals. Their positions for the isolated molecule result from solving the corresponding secular equation:<sup>46</sup>

$$\varepsilon_{MO}^{A/AB} = \varepsilon_a - \beta S \pm \beta \quad (23)$$

where  $\beta$  is the off-diagonal element and  $S$  is the overlap between the atomic orbitals of the two atoms of the molecule. Both parameters depend exponentially with the separation distance between the atoms  $r$ . Assuming the Wolfsberg – Helmholtz approximation<sup>47</sup> we have:

$$\beta = \langle a | \bar{V}_{aa'} | a' \rangle = -\beta_o e^{-r/l}; \quad S = \langle a | a' \rangle = -\gamma \beta \quad (24)$$

where  $l$  is a decay length and  $\beta_o$  is positive. The parameter  $\beta$  is attractive while  $S$  is repulsive, resulting in a Morse curve for the potential between the two atoms. The corresponding binding energy per electron is:

$$D_e = -\frac{1}{4\gamma} = \frac{\beta_o}{2} \quad (25)$$

Then we gather the terms containing the occupation numbers and redefine the position of the molecular orbitals as:

$$\begin{aligned} \tilde{\varepsilon}_{B,\sigma} = \varepsilon_a - 2\lambda q + U\langle n_{a,\sigma} \rangle - \alpha_{dip}(1 - \langle n_{a,\sigma} \rangle - \langle n_{a,-\sigma} \rangle) \\ \gamma\beta^2 + \beta = \tilde{\varepsilon}_{mol,\sigma} + \beta \end{aligned} \quad (26a)$$

$$\begin{aligned} \tilde{\varepsilon}_{AB,\sigma} = \varepsilon_a - 2\lambda q + U\langle n_{a,\sigma} \rangle - \alpha_{dip}(1 - \langle n_{a,\sigma} \rangle \\ - \langle n_{a,-\sigma} \rangle) + \gamma\beta^2 - \beta = \tilde{\varepsilon}_{mol,\sigma} - \beta \end{aligned} \quad (26b)$$

Note that now also appear the spin and image interactions. In this context the expression for the density of states of the molecule contains a term for the bonding and a term for the antibonding orbitals:

$$\begin{aligned} \rho_{mol} &= \sum_{\sigma} (\rho_{B,\sigma} + \rho_{AB,\sigma}) \\ &= \frac{1}{\pi} \sum_{\sigma} \left\{ \frac{\Delta}{(\varepsilon - \tilde{\varepsilon}_{B,\sigma} - \Lambda)^2 + \Delta^2} + \frac{\Delta}{(\varepsilon - \tilde{\varepsilon}_{AB,\sigma} - \Lambda)^2 + \Delta^2} \right\} \end{aligned} \quad (27)$$

In the case of weak interactions with the electronic levels of the electrode (wide band approximation) Eq. (27) has the form of two Lorentz distributions centred at the energies of the bonding and antibonding states (see Fig. 12). The integral of Eq. (27) up to the Fermi level gives the occupation of both, bonding and antibonding orbitals and in the case of the wide band approximation it is an analytical expression:

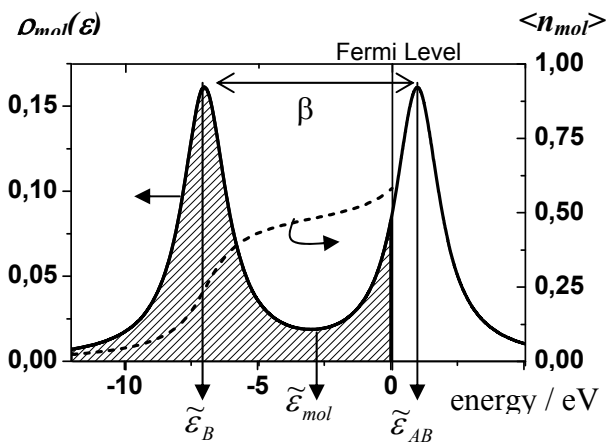


Figure 12. Density of states of the adsorbed molecule and the corresponding occupation obtained by integration according to Eqs. (27) and (28).

$$\begin{aligned}
 \langle n_{mol} \rangle &= \sum_{\sigma} \langle n_{B,\sigma} \rangle + \langle n_{AB,\sigma} \rangle \\
 &= \frac{1}{\pi} \sum_{\sigma} \left\{ \arg \left[ (\tilde{\varepsilon}_{mol,\sigma} + i\Delta)^2 - \beta^2 \right] \right\} \\
 &= \frac{1}{\pi} \sum_{\sigma} \left\{ \arg (\tilde{\varepsilon}_{B,\sigma} + i\Delta) + \arg (\tilde{\varepsilon}_{AB,\sigma} + i\Delta) \right\}
 \end{aligned} \tag{28}$$

where the argument has to be taken in the interval  $[0, 2\pi]$ . This is really a set of self-consistent equations, since  $\tilde{\varepsilon}_{mol}$  depends on the occupancy of the other spin orbital.

In this case the development of the density of states of the molecule as the reaction is proceeding, is the following: Initially, it has a filled bonding orbital lying well below the Fermi level, and an empty antibonding orbital well above (see Fig. 13). In the final state, the bond has been broken,  $B$  and  $AB$  orbitals have collapsed into a single orbital which is either empty and lies above  $\varepsilon_F$  for a

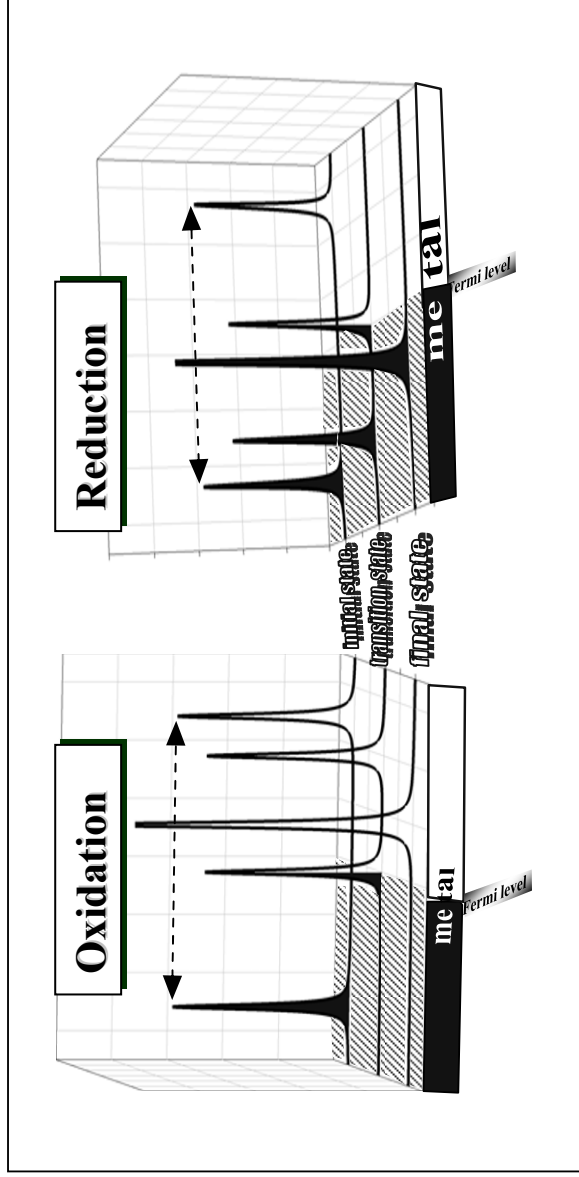


Figure 13. Evolution of the density of states of an adsorbed molecule in the absence of a *d band* for an oxidation reaction (left) and a reduction reaction (right).

oxidation reaction, or filled and lies below  $\varepsilon_F$  for a reduction reaction. For the reaction to proceed, a fluctuation of the solvent must shift the  $AB$  orbital below  $\varepsilon_F$  (for a reduction reaction) or the  $B$  orbital above  $\varepsilon_F$  (for an oxidation reaction). The critical phase (transition state) is when these orbitals actually pass the Fermi level. For the simple dissociation of the type:  $A_2 \rightarrow 2A$  without electron transfer, the distance between the atoms increases till they separate; at the same time, the interaction between the atoms is diminished, the separation between  $B$  and  $AB$  orbitals becomes smaller till it finally disappears. The position of  $\tilde{\varepsilon}_{mol}$  with respect to  $\varepsilon_F$  does not change during the reaction in this framework.

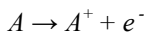
### VIII. 1-D AND 3-D POTENTIAL ENERGY REPRESENTATIONS

The way in which the rate constant is obtained from the general SKS-Hamiltonian<sup>15,16</sup> depends on the properties of the analysed system. In the simplest case where we consider that the interaction of the reactant with the electrode is weak, the expression for the energy of the system obtained from solving the Hamiltonian depends on the normalized solvent coordinate  $q$  according to Marcus – Hush model.<sup>10,11</sup>

$$\langle E(q) \rangle = \lambda q^2 + 2\lambda q + \tilde{\varepsilon}_a \langle n_a \rangle \quad (29)$$

where  $\tilde{\varepsilon}_a$  is given by Eq. (20).

Here it is illustrative to analyse as an example the reaction given in the first row of Table 1 (see also Fig. 14):



In the initial state we have a neutral species  $A$ , the occupation is  $\langle n_a \rangle = 1$ , the solvent coordinate  $q_{initial} = 0$  and the expectation value for the energy  $\langle E \rangle_{initial} = \varepsilon_\alpha$ . At the final state we have a cation  $A^+$ , the occupation is zero ( $\langle n_a \rangle = 0$ ), the solvent coordinate equal to the opposite of the charge of the species ( $q_{final} = -1$ )

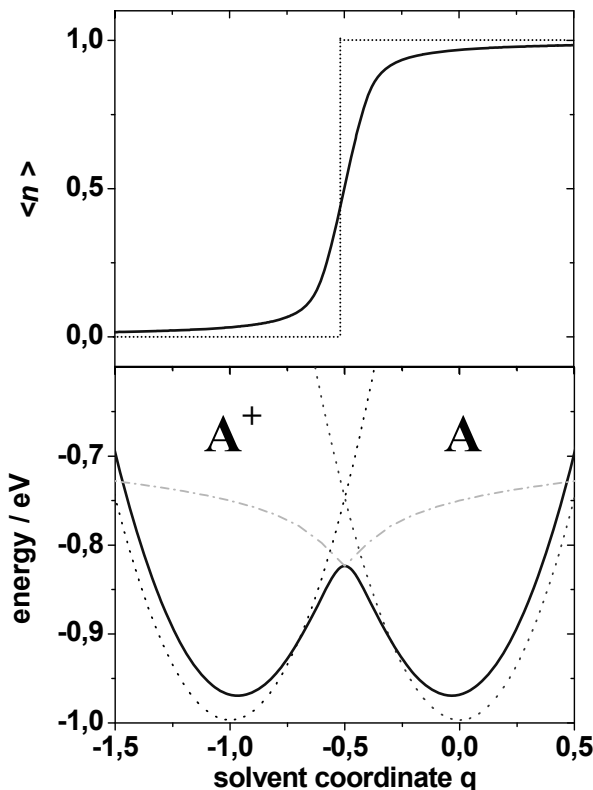


Figure 14. Occupation and adiabatic potential energy curves in thermodynamic equilibrium as a function of the solvent coordinate  $q$  for two limiting cases: strong interactions (full lines) and weak interactions (dotted lines). For the first case, it is also shown the electronic contribution (dotted dashed line, bottom plot).

and the expectation value of the energy  $\langle E \rangle_{final} = -\lambda$ . Then, the system is in thermodynamic equilibrium when  $\varepsilon_a = -\lambda$ . In this situation at the transition state the occupation is  $\langle n_a \rangle = 0.5$ , the solvent coordinate  $q_{trans} = -0.5$  and the expectation value for the energy  $\langle E \rangle_{trans} = \lambda/4 + \varepsilon_\alpha$  which gives the same activation energy

like Marcus – Hush model.<sup>10,11</sup> If an external potential is applied, the initial state is shifted according to Eq. (22).

When we consider the interactions with the electrode an additional term appears in Eq. (29) which is obtained by multiplying the density of states with the energy  $\varepsilon$  and then integrating up to the Fermi level:

$$\langle E_{elec} \rangle = \int_{-\infty}^{\varepsilon_F=0} \varepsilon \rho_a(\varepsilon) d\varepsilon \quad (30)$$

In the case of weak interactions, according to the wide band approximation an analytical expression for the total expectation of the energy is obtained:<sup>41</sup>

$$\langle E(q) \rangle = \lambda q^2 + 2\lambda q + \tilde{\varepsilon}_a \langle n_a \rangle + \frac{\Delta}{2\pi} \ln \frac{\tilde{\varepsilon}_a^2 + \Delta^2}{\varepsilon_a^2 + \Delta^2} \quad (31)$$

This equation gives the free energy curve of the reaction as a function of the solvent coordinate  $q$ . Figure 14 shows typical adiabatic potential energy curves in thermodynamic equilibrium for two limiting cases. For outer sphere reactions the level broadening  $\Delta$  is of the order of  $10^{-3}$ – $10^{-2}$  eV, and thus much smaller than the energy of reorganization  $\lambda$ , which is typically in the range of 0.5–1.0 eV. Then the term that accounts for the electronic contribution is negligible, the occupation probability of Eq. (21) becomes a step function and we have a parabola with a minimum at  $q = 0$  for  $A$  (initial state) and a parabola with a minimum at  $q = -1$  for  $A^+$  (final state). The crossing of the parabolas gives the activated state with coordinate  $q = -0.5$ . The electronic term produce a decrease of the energy, mainly at the barrier as can be appreciated from the dashed-dotted line in the figure (plot of last term of Eq.31).

In the case of simultaneous bond breaking and electron transfer, the contribution of the electronic interaction to the expectation value of the total energy can be also obtained from an equation similar to Eq. (30) but now involving the density of states of the molecular orbitals  $\rho_{mol}$ . Now we have to consider an additional coordinate, namely the separation between the atoms of the molecule which changes during the reaction. An analytical expression

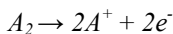
can be obtained for this term in the simplest case of wide band approximation:<sup>15,16</sup>

$$\begin{aligned} \langle E_{elec}(q, r) \rangle = \sum_{\sigma} \{ & \tilde{\mathcal{E}}_{B, \sigma} \langle n_{B, \sigma} \rangle + \tilde{\mathcal{E}}_{AB, \sigma} \langle n_{AB, \sigma} \rangle \\ & + \left[ \frac{\Delta}{\pi} \ln |\tilde{\mathcal{E}}_{B, \sigma} - i\Delta| + \frac{\Delta}{\pi} \ln |\tilde{\mathcal{E}}_{AB, \sigma} - i\Delta| \right] \} \end{aligned} \quad (32)$$

The total expectation value for the energy has contributions from the solvent, the spin and image interactions and the electronic term given by Eq. (32):

$$\begin{aligned} \langle E_{tot}(q, r) \rangle = & \lambda(q^2 + 2Zq) - 2U \langle n_{a, \sigma} \rangle \langle n_{a, -\sigma} \rangle \\ & + \frac{1}{2} \alpha_{dip} (1 - \langle n_{a, \sigma} \rangle - \langle n_{a, -\sigma} \rangle)^2 + \langle E_{elec}(q, r) \rangle \end{aligned} \quad (33)$$

The first term is the energy of the solvent when the spin orbitals are empty; the second and third terms avoid double counting for the Hartree Fock approximation. As an example, we chose the reaction of the fourth row of Table 1:



We consider a system where the molecule  $A_2$  is in equilibrium with two cations  $A^+$ . The resulting 3D-potential energy surface (left) and the corresponding occupation (right) are shown in Fig. 15 using the solvent coordinate  $q$  and the bond distance  $r$  as reaction coordinates. A minimum centered at  $q = 0$ ,  $r = r_o$  corresponding to the molecule and a valley centered at  $q = -2$  related to the two cations are clearly observed; both regions are separated by an energy barrier. The occupation probability shows the expected behaviour:  $\langle n_{tot} \rangle = 2$  and  $\langle n_{tot} \rangle = 0$  for the molecule and the two cations respectively. At the bottom of the figure are the projected 2-D contour plots. We will often employ this 2-D type of representation. Within our model the potential energy can be calculated for different reactions. Figure 16 shows contours plots of such poten-

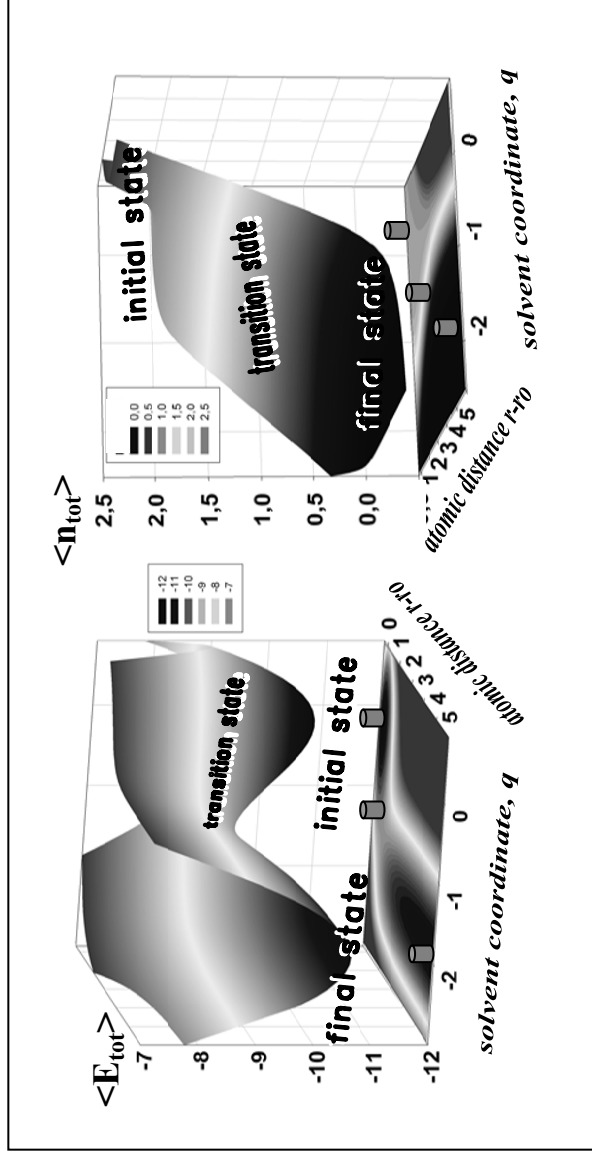


Figure 15. Adiabatic potential energy and occupation surfaces in thermodynamic equilibrium as a function of the solvent coordinate  $q$  and the separation distance  $r-r_0$  between the atoms of the molecule for an oxidation reaction with simultaneous bond breaking. At the bottom the contour projection of the 3D-surfaces are shown.

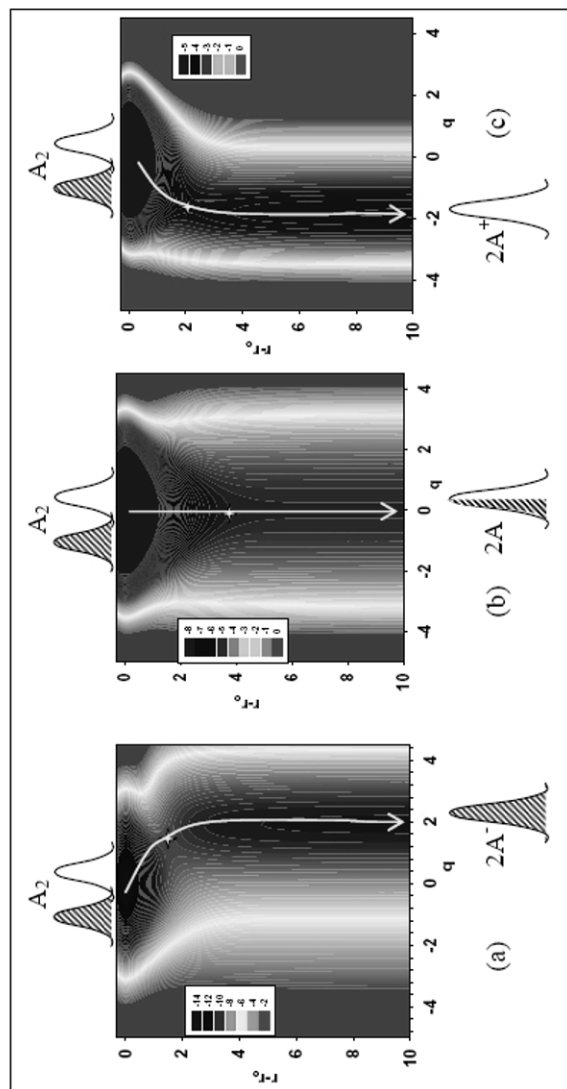


Figure 16. Contour projection of the 3D-adiabatic potential energy surfaces in thermodynamic equilibrium as a function of the solvent coordinate  $q$  and the separation distance  $r-r_0$  between the atoms of the molecule for three different cases: a reduction, a dissociation and an oxidation reaction with simultaneous bond breaking. (Data obtained from Ref. 45.)

tial energy surfaces at a fixed distance of the reactant to the electrode for three different cases: the reduction of a molecule (a), the dissociation without electron transfer (b), and the oxidation (c). In all the cases we can follow the energy of the system and the occupation of the molecular orbitals along the whole reaction path. The initial state is a neutral molecule corresponding to a minimum at the solvent coordinate  $q = 0$ , and with the bond distance at its equilibrium value  $r = r_o$ . The reaction goes through a saddle point (marked by a star) to the valley at a higher bond distance centered at a solvent coordinate  $q_f$ , which is different in the three cases considered. In the first case, the reduction of the molecule produces two anions (a). Then the valley at higher separation between the atoms is centred at  $q_f = +2$ . For the dissociation of the molecule to two atoms, the center of the final valley is located at  $q_f = 0$ , and in (c) the molecule is oxidized to two cations with the valley at  $q_f = -2$ . In all cases the system has to overcome a saddle point situated at an intermediate value of the solvent coordinate  $q$  and the bond distance  $r$ . We note that the surfaces in this figure are meant to demonstrate the typical reactions paths, therefore they have been calculated for a constant chemisorption function  $\Delta$ , which corresponds to the non-catalytic coupling to a  $sp$  wide band and to the absence of a  $d$  band. Model calculations performed for reactions on a metal surface in the gas phase, which can nowadays be routinely performed with the aid of quantum-chemical packages, can only describe the pure dissociation  $A_2 \rightarrow 2A$ , but not electron transfer with bond breaking. They may still illuminate certain aspects of these reactions, but are necessarily incomplete.

## IX. ELECTROCATALYSIS BY A NARROW $d$ BAND

The wide band approximation can be applied to describe very well the behaviour of metals with large, structureless  $sp$  bands. However, the more interesting materials showing electrocatalytic properties, such as platinum or ruthenium, possess narrow  $d$  bands. Then the next step in the development of the model is to abandon the wide band approximation and consider the electronic structure of the bands.<sup>43-45</sup> Next, we discuss the superposition of a wide  $sp$

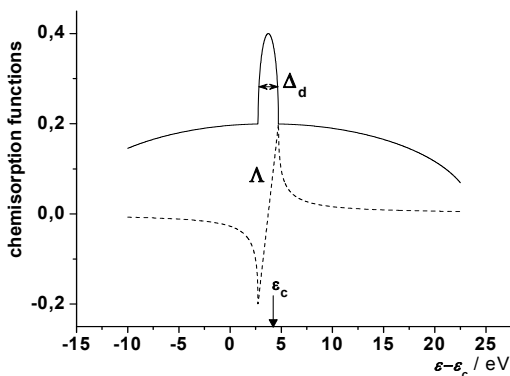


Figure 17. Chemisorption functions  $\Delta$  and  $\Lambda$ , for the semielliptic model in the case of a superposition of a wide *sp* band and a thin *d* band.

*band* and a narrow *d* band. It is convenient to use semielliptical shapes for which several important properties can be calculated explicitly (Fig. 17):<sup>43-45</sup>

$$\Delta_{Total}(\varepsilon) = \Delta_{sp}(\varepsilon) + \Delta_d(\varepsilon) \quad \text{and} \quad \Lambda_{Total}(\varepsilon) = \Lambda_{sp}(\varepsilon) + \Lambda_d(\varepsilon) \quad (34)$$

Equation (16) contains contributions from both the *sp* and the *d* band. Now it is no more possible to obtain an analytical expression for the occupation of the electronic states of the reactant, nor for the corresponding energy. However, the integrals in Eqs. (21) and (30) can be easily calculated numerically. Figure 18 shows the electronic contribution of the energy in the case of the superposition of a wide *sp* band with a narrow *d* band ( $w_d = 1$  eV) with a coupling constant  $|V_{eff}| = 1.6$  eV<sup>2</sup> located at the Fermi level in comparison with the effect observed in the absence of the *d* band. In both cases the orbital is half occupied; however by the presence of the *d* band it is elongated to lower values of energy. This effect produces that the electronic contribution given by the integral up to the Fermi level of the product between the energy coordinate  $\varepsilon$  and the density of states of the reactant  $\rho_a$  (Eq. 30) becomes more

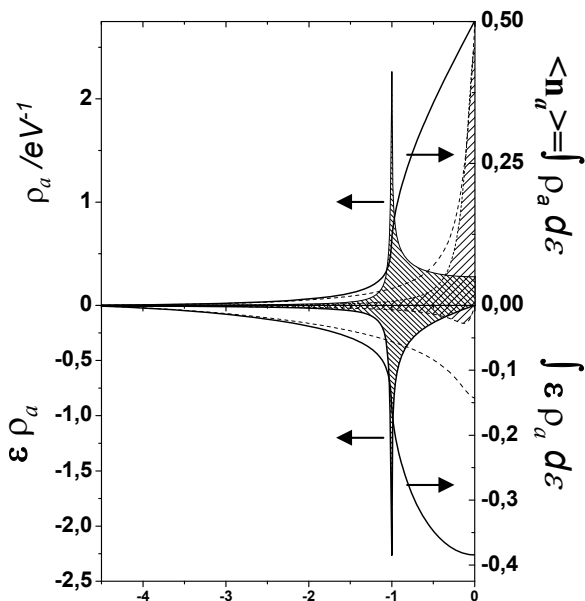


Figure 18. Upper plot: density of states of the adsorbate  $a$  and the corresponding occupation obtained by integration according to Eq. (21) for the semielliptic model in the case of a superposition of a wide  $sp$  band and a thin  $d$  band (full lines) in comparison with the case in the absence of the thin  $d$  band (dotted lines). Bottom plot: the corresponding illustration for the determination of the electronic contribution according to Eq. (32).

negative than in the absence of the narrow  $d$  band. Also, one notices a sharp peak at the border of the band that accounts for a binding with the electrode. Figure 19 is similar to Fig. 13 and shows the development of the states of the molecule for the oxidation and the reduction reactions but now when a strong interaction with a narrow  $d$  band centered almost at the Fermi level takes place. The initial state corresponds to the molecule, where the density of states shows the familiar splitting into bonding below (filled) and antibonding states above the Fermi level (empty) according to Eq. (27). During the bond breaking the atoms of the

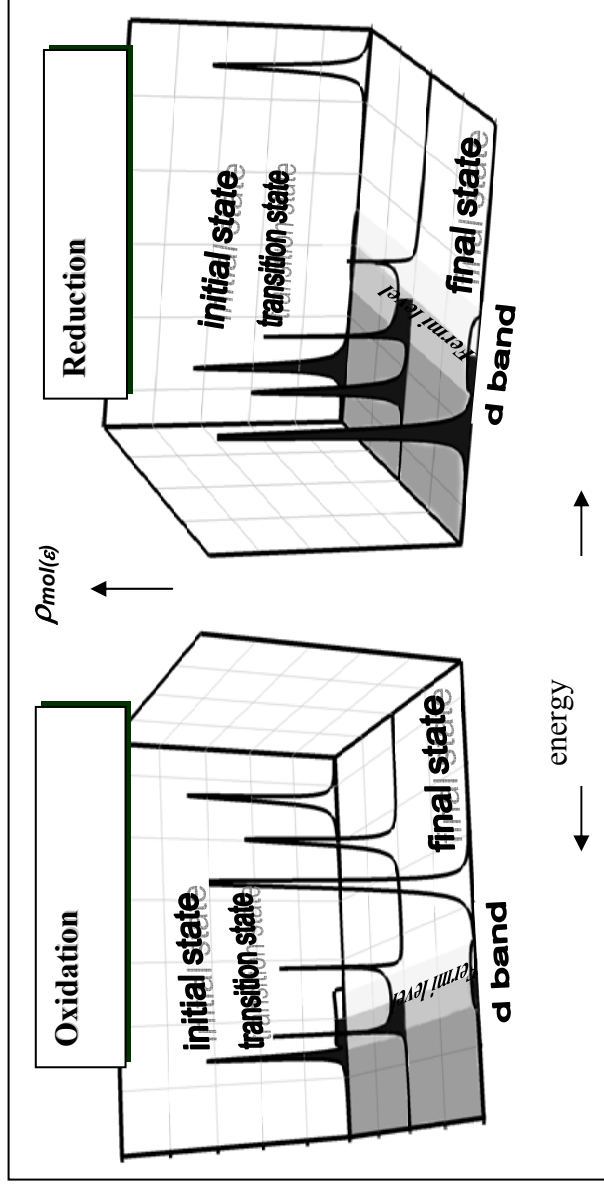


Figure 19. Evolution of the density of states of an adsorbate in the presence of a thin *d band* localized near the Fermi level for an oxidation reaction (left) and a reduction reaction (right).

molecule are separated and the energies of  $B$  and  $AB$  become closer. In the transition state the  $B$  ( $AB$ ) orbital crosses the Fermi level for the oxidation (reduction) reaction, and due to the strong interaction with the narrow  $d$  band the orbital is elongated and split as described previously, thus decreasing the energy at the barrier. In the case of the oxidation the  $B$  orbital becomes partially empty while in the reduction reaction the  $AB$  orbital is partially filled. In the final state the bond has been broken, the atoms are separated, and  $B$  and  $AB$  orbitals have collapsed into single empty (filled) orbital lying above (below) of the Fermi level for the oxidation (reduction) reaction. Figure 20 shows the adiabatic potential energy surfaces obtained for the two cases described above. The decrease in the activation barrier by the presence of a narrow  $d$  band is evident. Then, in order to have an electrocatalytic effect, it is crucial to have a strong interaction of the molecular orbitals when they are passing the Fermi level. However, it is not only the position of the band but also other factors play a role in the mechanisms of decreasing the activation barrier.

Next we analyse the effects of different parameters for the interaction of the  $d$  band with the  $AB$  orbital at the saddle point for the reduction reaction (Fig. 21). An important factor is the coupling constant  $|V_{eff}|^2$ , which is a measure of the overlapping between the reactant and the electrode. For a weak interaction, the  $AB$  states just gets broadened (upper left); with increasing strength it splits into two states: one that is bonding, and one that is antibonding with respect to the electrode. The bonding part lies substantially below the Fermi level and thus reduces the energy of the activated state. The center panel shows the effect of the width of the band: for a very large width, cantered at the Fermi-level, the  $AB$  peak gets smeared into a single, very broad peak. The panel at the right shows the effect of the position of the  $d$  band center. Obviously, a position near the Fermi-level is optimal. However, there is some asymmetric behaviour according to the type of reaction as can be observed from Fig. 22 (left). For the case of the oxidation the optimal position lies about 1 eV below the Fermi level for these conditions, while for the reduction it lies a little above. The dissociation reaction shows the major reactivity when the  $d$  band is positioned exactly at the Fermi level and the behaviour is symmetric around the Fermi level. For the case of the reduction, Fig. 22 (right) also shows, how the energy of activation varies as a func-

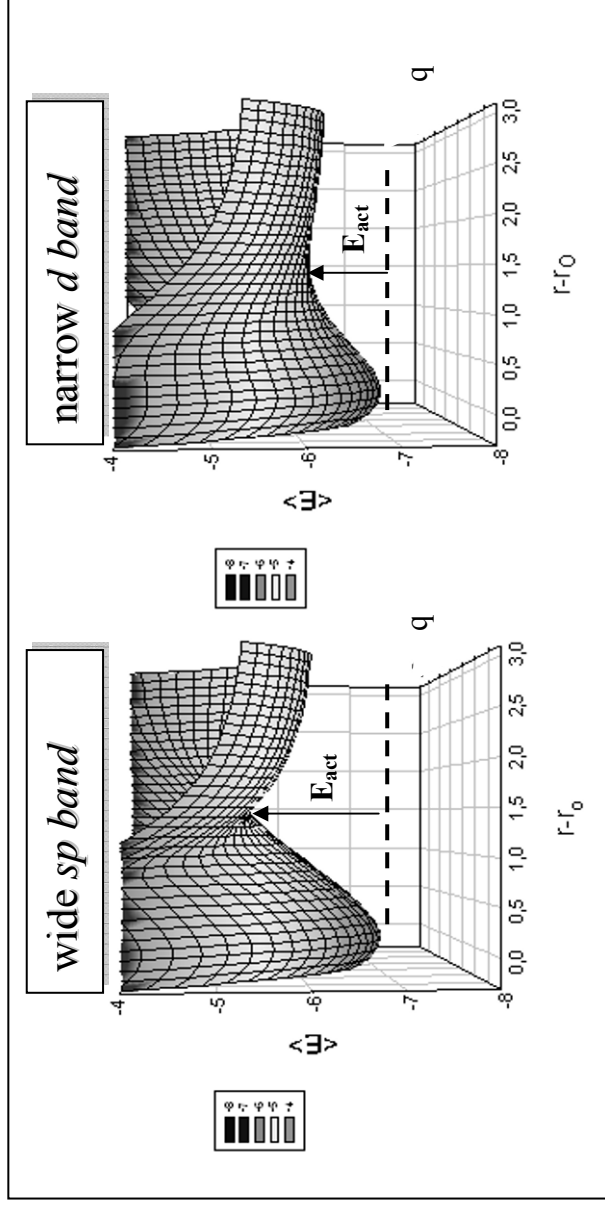


Figure 20. Adiabatic potential energy surfaces showing the decrease of the activation barrier produced by the presence of a narrow *d* band near the Fermi level.

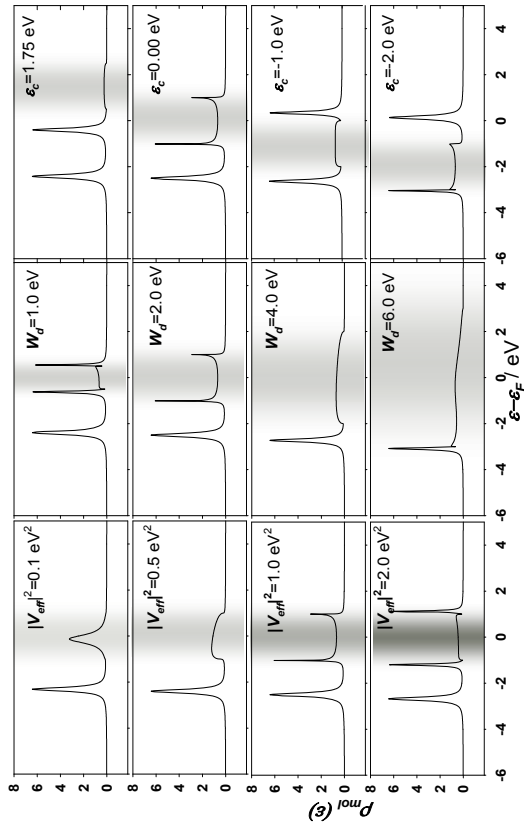


Figure 21. Effect of different parameters of the  $d$  band on the density of states at the saddle point. Left: effect of the coupling constant. Center: effect of the width. Right: effect of the position of the center of the band. (Data obtained from Ref. 44.)

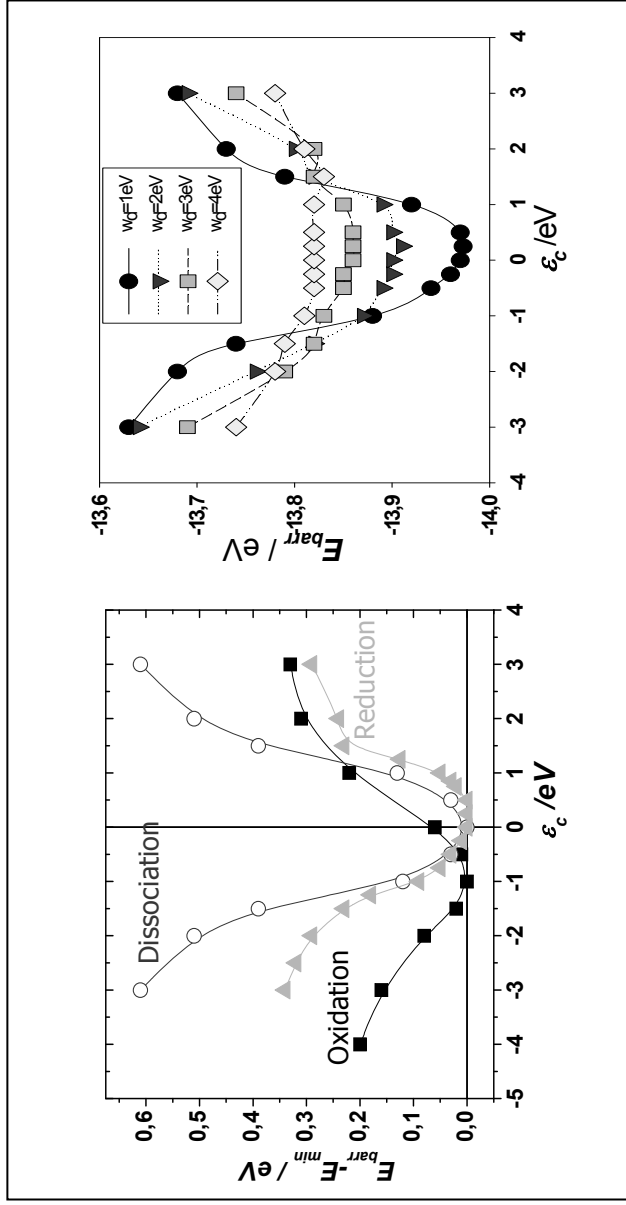


Figure 22. Left: Effect of the position on the activation barrier of a narrow *d band* for an oxidation (squares), a dissociation (circles) and a reduction (triangles) reaction. Right: Effect of the width of the band on the activation barrier for a reduction reaction.

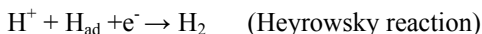
tion of the position of the band center for various width. For a band centered near the Fermi level, a narrow width is favourable, while for a band far from  $\varepsilon_F$  a wider band is more favourable, which still reaches  $\varepsilon_F$ . It is important to take into account these effects in the design of electrocatalysts in the nanoscale range. It is well known that the introduction of some defects such as steps or the formation of clusters change the electronic properties of the electrode materials (see Sections below). Considering the examples of Fig. 22, a shift of the position of the  $d$  band to lower energies than the Fermi level (in this example from 0 to  $-1$  eV) should improve the activity for the oxidation reaction but inhibit the reduction.

## X. APPLICATION TO REAL SYSTEMS – HYDROGEN EVOLUTION / OXIDATION REACTIONS

Calculations with idealized band shapes are very useful for understanding the mechanism of electrocatalysis,<sup>43,44</sup> but to predict the activity of real systems we need the *real* density of states of the metal and the corresponding coupling constant with the reactant. We have chosen as an illustrative example the hydrogen oxidation because it is one of the fundamental reactions of electrochemistry. It is the reaction which occurs at the anode of fuel cells and because of its relative simplicity, it is often considered to be the prototype of an electrocatalytic reaction, whose rate depends strongly on the nature of the electrode material as mentioned at the beginning of this chapter. Thus, we focus on the electrocatalytic activity of different materials and nanostructures for this reaction and its reverse, the hydrogen evolution. The latter occurs in two steps, mostly via the Volmer-Tafel mechanism:<sup>48</sup>



The Tafel reaction has an alternative, the Heyrowsky reaction:



According to the energy balance the oxidation of hydrogen requires almost 32 eV; about 22 eV are provided by the hydration of the proton, 9–10 eV, twice the work function, by the metal, and the rest by the potential drop between the electrode and the bulk of the solution, which is the only part that we can control experimentally. Thus, solvation plays a dominant part in the energetics, and any model for the hydrogen reaction that neglects the solvent leaves out a most important part.

Figure 23 shows the *d band* densities of states of nine different metals. The position and the shape of the *d bands* differ widely. Ir and Re have wide bands centered almost at the Fermi level. The bands of Ni, Co and Pt are somewhat thinner, but with a higher density of states at  $\varepsilon_F$ . Rh is an intermediate case between these two groups. On the other hand, the coin metals Ag, Cu and Au have very thin bands with a high density of states at its centre, but they are localized several eV below  $\varepsilon_F$ . The coupling constants, which are given in the same figure,<sup>23</sup> are very different from one metal to the other and there is no correlation with the features of the bands. They depend on the extension of the orbitals, and thus increase when going down a column of the periodic table. The rate determining steps of the hydrogen evolution reaction may also be different for the various metals. In a first step we have calculated the activation energy for the hydrogen oxidation reaction applying our model according to the Hamiltonian of Eq. (5). The density of states for the metal and the corresponding coupling constant were obtained from DFT calculation. The interaction between the hydrogen atoms were regarded within the Hückel approximation (Eqs. 23–25). The obtained results are shown in Fig. 24. Here the experimental results compiled from<sup>3,4</sup> for the exchange current density are plotted versus the activation energy calculated from our model.<sup>45,49</sup> Except for Au and Ag, the experimental values in the literature vary by at most one order of magnitude. This is the kind of variation to be expected when different measuring techniques or different surfaces are used. Several of the data are 40–50 years old, but since that time there has been no significant advance in the measurement of kinetics, so the variation of the rate over six orders of magnitude is real. Where there has been a significant advance is in the pretreatment of noble metal electrodes by flame annealing.<sup>50</sup> This may explain the large discrepancy in the data for gold and silver. The data point with the high exchange current for

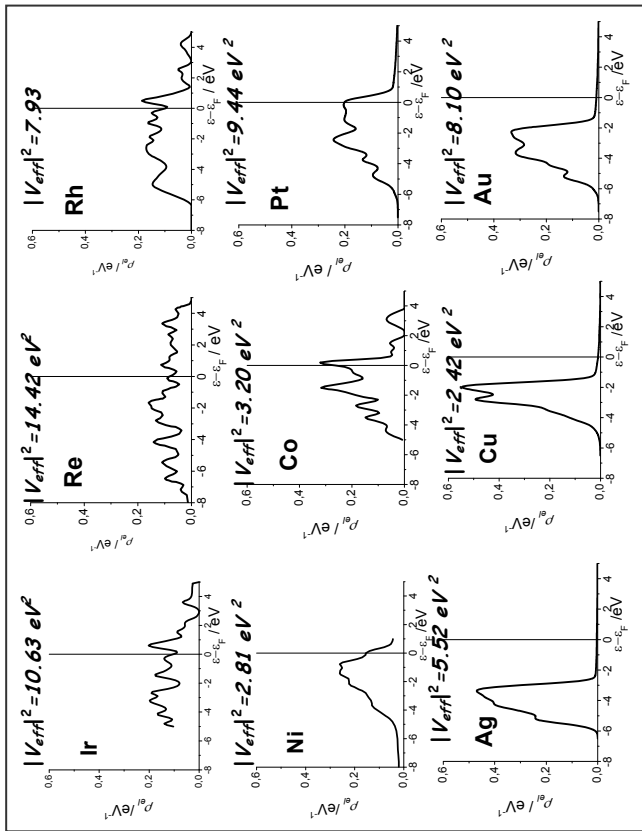


Figure 23. Density of states for different metals obtained by DFT calculations and the corresponding coupling constants taken from Ref. 23. (Data obtained from Ref. 45.)

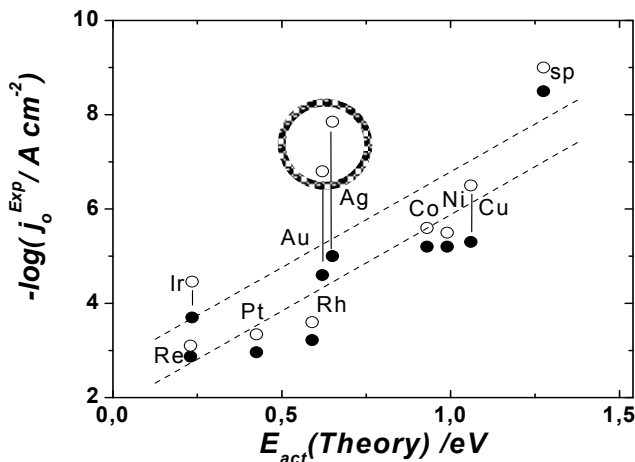


Figure 24. Correlation between experimental (compiled from Refs. 3 and 4) and theoretical results for the hydrogen oxidation reaction at different metal electrodes. The circle surrounds data without flame treatment. (Data obtained from Refs. 45 and 49).

silver was measured in our laboratory by pulse methods and with the flame treatment.<sup>51,52</sup>

## XI. DFT QUANTUM CHEMICAL CALCULATIONS AS INPUT FOR THE SKS-HAMILTONIAN

Now we go a step forward and combine the developed model for electrocatalysis with results of quantum chemical calculations to investigate the effect of the electrode's electronic structure on the rate of the hydrogen oxidation reaction in a more realistic way.<sup>53-55</sup>

We consider just one reactant orbital interacting with the metal surface; in the model calculations reported below this will either be the 1s orbital of the hydrogen atom or the bonding orbital of the  $\text{H}_2$  molecule. Also, we include neither the Coulomb repulsion  $U$  between two electrons on the same orbital nor the dipole-dipole interaction term originated by the image charge, since those will be handled by DFT calculations. Also, we abandon the Hückel ap-

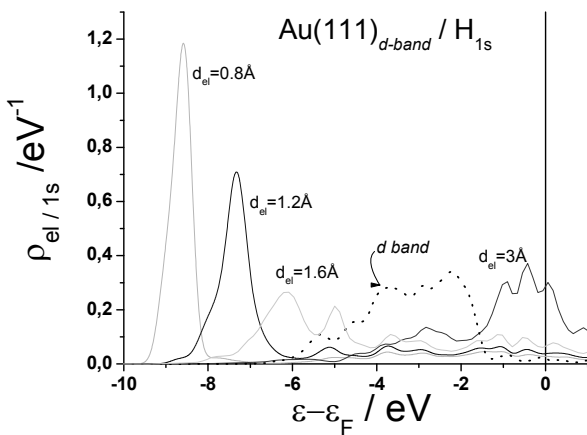


Figure 25. Projected density of states on the  $d$  band of Au(111) (dotted line), and on the  $1s$  orbital of hydrogen when the atom approaches to the surface (Data obtained from Ref. 55.)

proximation to treat the molecular bond and consider the interaction between the atoms in the DFT framework. We start considering the Volmer reaction, the first step of the hydrogen evolution reaction. 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. There are several possible sites at the surface where the hydrogen atom can adsorb. For the fcc metals Pt, Au, Ag, Cu, the optimum position for hydrogen adsorption was always the fcc three-fold hollow site; for Cd(0001) it was the threefold hollow site. Next we performed calculations of the projected density of states on the  $sp$  and  $d$  bands of the metal and on the  $1s$  orbital of the hydrogen atom by means of the DFT formalism at different distances to the electrode. Figure 25 shows as an example the results obtained for the adsorption on Au(111). This situation corresponds to a solvent coordinate of  $q = 0$ . Since the hydrogen atom is completely discharged solvation effects are absent. Then we obtain the parameters  $\Delta$ ,  $\Lambda$  and  $\tilde{\epsilon}_a$  by fitting according to Eq. (17), and the electronic energy that we will call  $E_{DFT}$ . Figure 26 shows the fitted parameters  $|V_{eff}|^2$  and  $\tilde{\epsilon}_a$  for

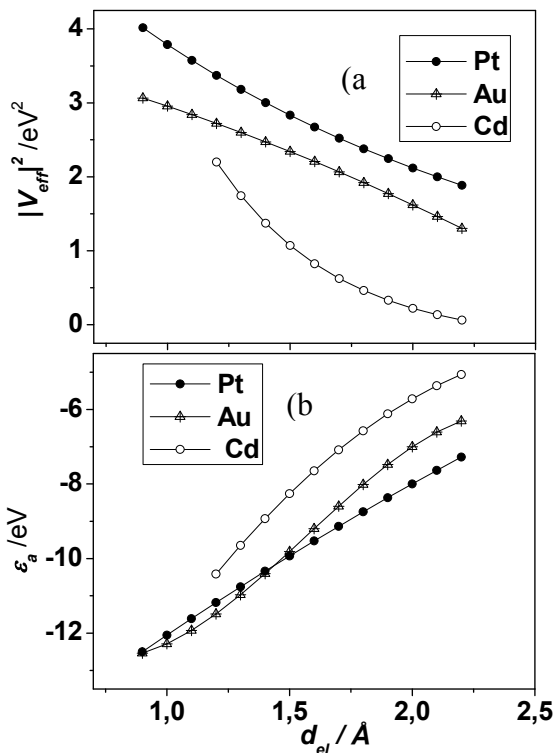


Figure 26. Interaction constants  $|V_{eff}|^2$  as a function of the distances for the three selected metals, (a) and the hydrogen level  $\varepsilon_a$  as a function of the distances  $d_{el}$  to the surface for the metals investigated (b), taking the vacuum as the reference level. (Data obtained from Ref. 55.) The normalization of the coupling constants differs by a factor of pi compared with those given in Fig. 23.

the three selected examples (Pt, Au and Cd). As expected,  $|V_{eff}|^2$  decreases in the order  $\text{Pt} > \text{Au} > \text{Cd}$ , and fall off with the distance. 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

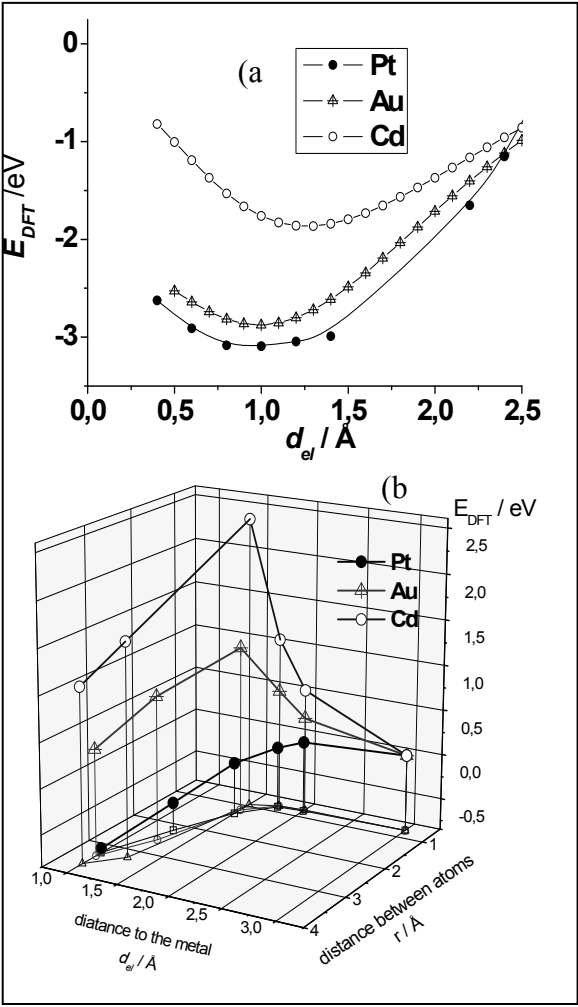


Figure 27. Energy of an adsorbed H atom as a function of distance  $d_a$  to the surface (a) and of an adsorbed H<sub>2</sub> molecule as a function of the bond length  $r$  and of the distance  $d_{el}$  to the surface (b). (Data obtained from Refs. 53 and 55.)

effect. The hydrogen level  $\tilde{\varepsilon}_a$  increases with distance, 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 behaviour of the *sp bands* differs little between these metals.

Figure 27 shows the energy for the adsorption of a hydrogen atom (a) and for the dissociation of a hydrogen molecule (b) at different distances to the electrode for three different metals, Cd(0001) (a bad catalyst), Au(111) (a mediocre catalyst) and Pt(111) (an excellent catalyst). In the case of the dissociation of the hydrogen molecule, as the distance to the surface decreases, the separation between the two hydrogen atoms increases, until they are finally adsorbed in the threefold fcc hollow sites. On platinum, hydrogen dissociates practically without a barrier, on gold and cadmium dissociation is unfavourable and further requires the passing of an energy barrier; both the barrier and the energy of the adsorbed atom are much higher on cadmium than on gold.

We calculate the electronic energy  $E_{model}$  according to our model for the same configuration (for  $q = 0$ ) from Eq. (30), the difference  $\Delta E$  between the results obtained by DFT and the integral of Eq. (30) is the exchange and correlation part that is now considered in a more realistic way than the Hartree Fock approximation for the spin and dipole-dipole interaction of the image charge:

$$\Delta E(q=0) = E_{model}(q=0) - E_{DFT} = \int_{-\infty}^{E_F} \varepsilon \rho_{1S} d\varepsilon - E_{DFT} \quad (35)$$

Because of its high ionization energy the adsorbed hydrogen is neutral on all metals, i.e., the occupation of the hydrogen orbital  $1s$  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 when the proton is formed. In the latter case the electronic energy also vanishes. We therefore use the following procedure: In order to obtain this cor-

reaction for arbitrary values of  $q$ , we assume that it is proportional to the occupation of the hydrogen orbital:

$$\Delta E(q) = \Delta E(q=0) \langle n_{1s} \rangle \quad (36)$$

Thus we use this linear interpolation to extrapolate the DFT results, which are valid for  $q=0$ , to other values in the range  $0 \leq q \leq 1$ .

The interactions that are missing in DFT are those of charged species with the solvent. Then, we have to consider the energy of the proton with its environment. The energy of the proton would be just  $-\lambda$ , but this is only the interaction with the slow solvent modes. The parts corresponding to the fast solvent modes, the image force, and its interaction with the electrostatic potential must be considered. Fortunately, we do not have to calculate them explicitly, since we know that at the equilibrium potential the free energy of the proton must be one half of the free energy  $E_{H_2}$  of the hydrogen molecule. Therefore we write:

$$E_{fast} = (1 - \langle n_{1s} \rangle) \left( \frac{E_{H_2}}{2} + \lambda \right) \quad (37)$$

where the interaction has been assumed to be proportional to the charge. The energy of the  $H_2$  molecule is  $-31.73$  eV, and the entropic contribution is  $-0.41$  eV,<sup>3</sup> which gives:  $\Delta G_{H_2} = -32.11$  eV. Again, we have used a simple and natural interpolation.

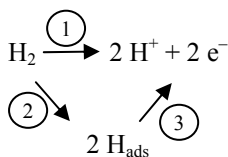
Then, the total energy is the sum of the electronic energy calculated from Eq. (30) corrected by Eq. (36) and the solvent energy both, slow and fast contributions:

$$E_{total} = \int_{-\infty}^{E_F} \varepsilon \rho_{1s} d\varepsilon + \Delta E(q) + \lambda q^2 + 2\lambda q + E_{fast} \quad (38)$$

$\rho_{1s}$  contains the fitted parameters  $\Delta$ ,  $\Lambda$  and  $\tilde{\varepsilon}_a$  corrected by the solvent term  $2\lambda q$  and the overpotential  $e_o \eta$ .

Now we can calculate the adiabatic potential free energy surfaces as a function of the solvent coordinate  $q$  and the distance to

the electrode  $d_{el}$  for the Volmer reaction. Similar calculations can be also performed for the overall reaction  $H_2 \rightarrow 2 H^+ + 2 e^-$ . However, here we have to take into account, that when the molecule approaches to the surface of the electrode, the distance between both hydrogen atoms simultaneously changes. As an example, both surfaces are shown in Figs. 28a and 28b for these reactions on Au(111). We show the energy as a function of the solvent coordinate  $q$  and the distance to the metal  $d$  for the Volmer reaction and as a function of the solvent coordinate  $q$  and the interatomic separation  $r$  for the overall reaction. In the latter case, we have to keep in mind that actually we have a third coordinate, i.e., the distance to the electrode. The distance between both atoms when the molecule approaches to the electrode, decreases as a consequence of the dissociation reaction (see Figure 27b). In Fig. 28a, at  $q = 0$  and  $r = 0.76 \text{ \AA}$ , we observe a minimum corresponding to the stable molecule; the valley centered at  $q = -2$  corresponds to  $2H^+$ . The direct oxidation of the molecule would require an activation energy of about 1.8 eV, the dissociation requires about 1.15 eV and is therefore favoured, even though it leads to an intermediate state with a higher energy. For the subsequent oxidation, we have to take into account that this diagram is for the simultaneous oxidation of two hydrogen atoms, which is less favourable than a consecutive oxidation of two atoms. Therefore we can infer from these results that the preferred mechanism is first the dissociation of the hydrogen molecule and then the oxidation of the adsorbed atom to proton but the reaction for the second step has to be calculated separately. We can represent these processes through the following diagram:



In Table 2 are summarized the energetics values for the different steps shown in this schema. We have considered for all the cases that the reaction (1) is in equilibrium, so its  $\Delta G = 0$ .

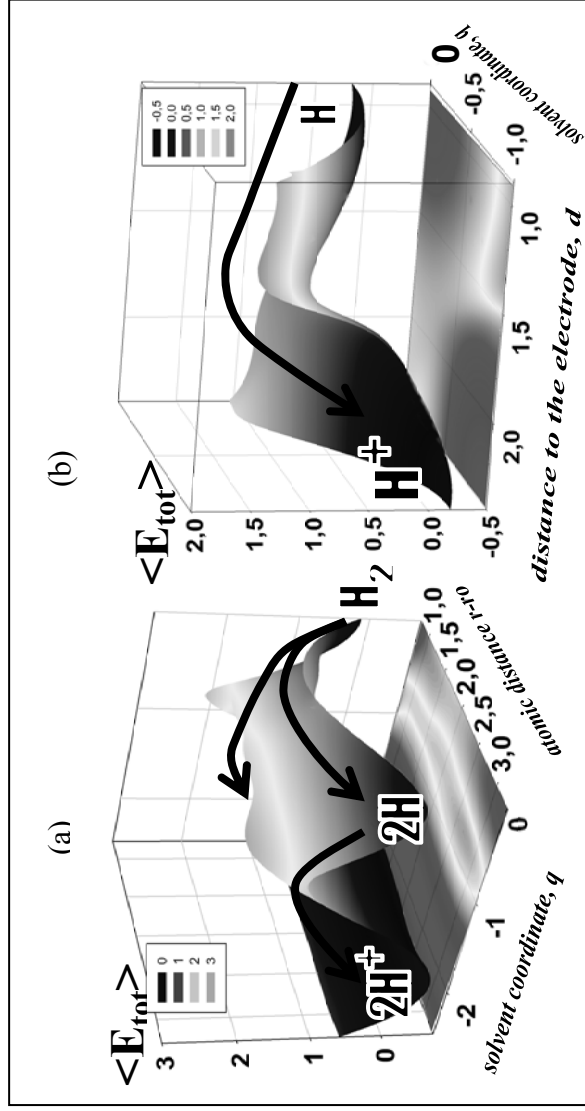


Figure 28. Adiabatic potential energy surfaces in thermodynamic equilibrium as a function of the solvent coordinate  $q$  and the separation distance  $r\text{-}r_0$  between the atoms of the molecule for the overall reaction (a) and as a function of the solvent coordinate  $q$  and the distance  $d_e$  of the hydrogen atom to the surface for the Volmer reaction (b). At the bottom are shown the contour projection of the 3D-surfaces.

**Table 2**  
**Energetics Values for the Different Steps of the Hydrogen Reaction According to the Schema Shown in the Text.**

| Electrode | $\Delta G_{\text{barrier}}$ | $\Delta G_{\text{reaction}}$ | Reaction                                           |
|-----------|-----------------------------|------------------------------|----------------------------------------------------|
| Cd        | 2.0                         | 0.91                         | $\text{H}_2 \rightarrow 2 \text{H}$                |
| Au        | 1.15                        | 0.41                         |                                                    |
| Pt        | 0                           | -0.25                        |                                                    |
| Cd        | 6.0                         | 0                            | $\text{H}_2 \rightarrow 2 \text{H}^+ + \text{e}^-$ |
| Au        | 1.8                         | 0                            |                                                    |
| Pt        | 1.75                        | 0                            |                                                    |
| Cd        | 0.90                        | -0.91                        | $\text{H} \rightarrow \text{H}^+ + \text{e}^-$     |
| Au        | 0.70                        | -0.41                        |                                                    |
| Pt        | 0.27                        | 0.25                         |                                                    |

## XII. ELECTROCATALYSIS AT NANOSTRUCTURES

It is well known that different nanostructures show different electrocatalytic properties. There is in the literature sufficient experimental evidence<sup>56-60</sup> that clusters, steps, decorated steps, deposition of monolayers or submonolayers of foreign metals on different substrates can increase or inhibit the velocity of electrochemical reactions. Indeed, electrochemistry offers convenient means to generate various nanostructures such as metal overlayers, steps decorated by adatoms, or even monoatomic nanowires. The big scientific challenge is to understand, how the structure affects the chemical and physical properties of the materials, and how this in turn influences their reactivity. Although some empirical correlations have been successful and some DFT calculations for the gas phase have been extended to electrochemical systems, there is a lack of fundamental explanations. The theory that we have applied in the previous Sections to flat surfaces can be extended to nanostructures and preliminary results are promising. Figure 29 shows some of the different nanostructures for which we are performing calculations. There are several nano-scale and geometrical effects, such as electronic changes arising due to strain in the lattice of the supported metal generated from the bigger/smaller lattice constant

of the substrate. For the reactive properties of metal electrodes the position and the width of the *d bands* are important. Thus, the *d-band* position can be changed due to *expansion* or *compression* of the lattice constant. As expected, in the case of nanowires, the interatomic spacing is shorter than in the bulk metals.<sup>61</sup> Because of the smaller number of neighbours, the *d bands* are much narrower than at surfaces, and show more pronounced peaks. Also the work functions are considerably larger in the wires, this effect being particularly large for gold. The large shift in the work function implies that the wires carry a negative excess charge in the hydrogen evolution region.<sup>62</sup> As an example, Fig. 30 a-b shows the effect of the nanostructures on the electronic properties of the electrodes. The electronic structures of the *d bands* of Au and Pd are strongly influenced by the geometric structures of the material. These two examples are paradigmatic. Au as a flat surface is a mediocre electrocatalyst while as a wire the density of states shift up to the Fermi level. In the latter case the activation barrier for the hydrogen oxidation decreases from 0.7 eV for the flat surface down to 0.1 eV!<sup>61</sup> as can be appreciated from Fig. 31. This effect can be also qualitatively explained in the following way: On a flat surface, the *d band* lies well below the Fermi level. In the wire, this is significantly shifted to higher values, and ends right at the Fermi level. Therefore, a part of the antibonding density of states of the hydrogen orbital now also extends above the Fermi level and is unfilled, so that the *d band* now contributes to the bonding. In the case of Pd deposited on different substrates, the largest effect occurs for the cluster. Here the density of states is strongly shifted towards the Fermi level, with a pronounced peak lying just below the Fermi level. On the monolayer, the density of states is also strongly shifted towards the Fermi level, but the effect is not quite as large as for the cluster. These shifts are qualitatively well explained by the *d band* model of Hammer and Nørskov.<sup>23</sup> Since the lattice constant for the monolayer is smaller than for the bulk, the width of the *d band* is reduced. Since the total occupation of this band does not change, its center has to move towards the Fermi level. The hydrogen oxidation is about 2-3 order of magnitude

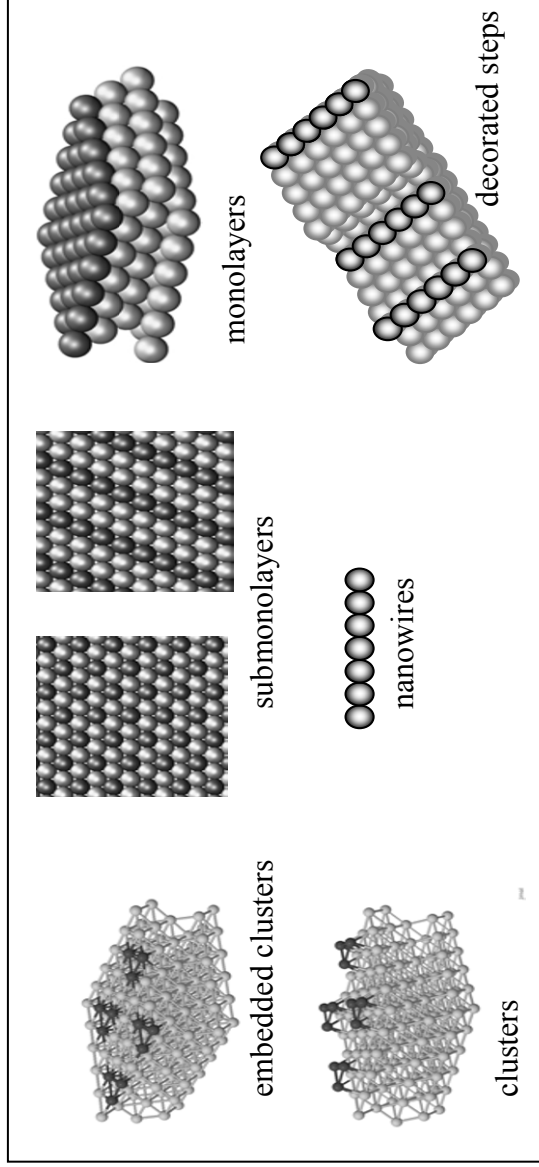


Figure 29. Different nanostructures of foreign metals deposited on different substrates.

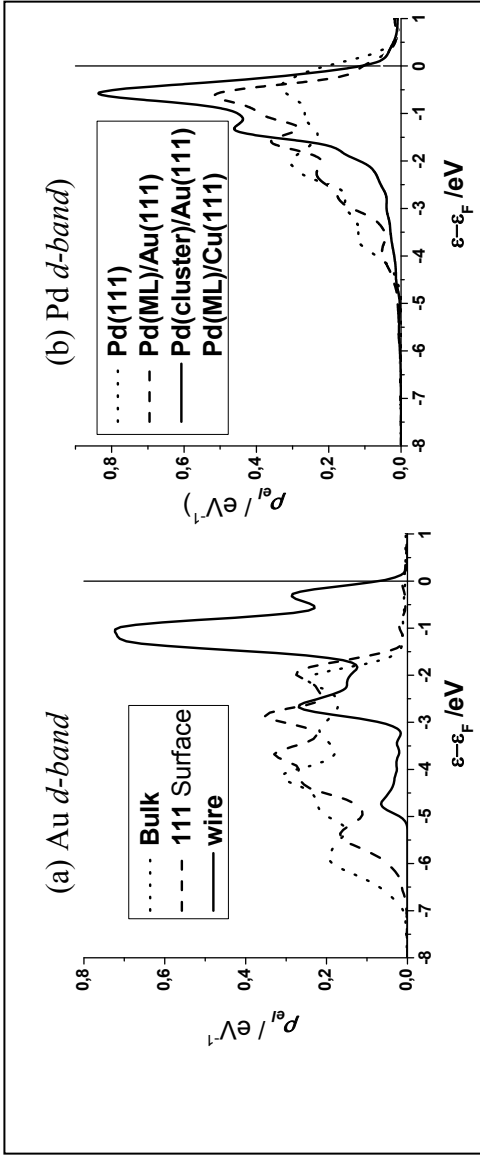


Figure 30. Density of states corresponding to the  $d$ -band of different nanostructures of Au (a) and Pd (b).

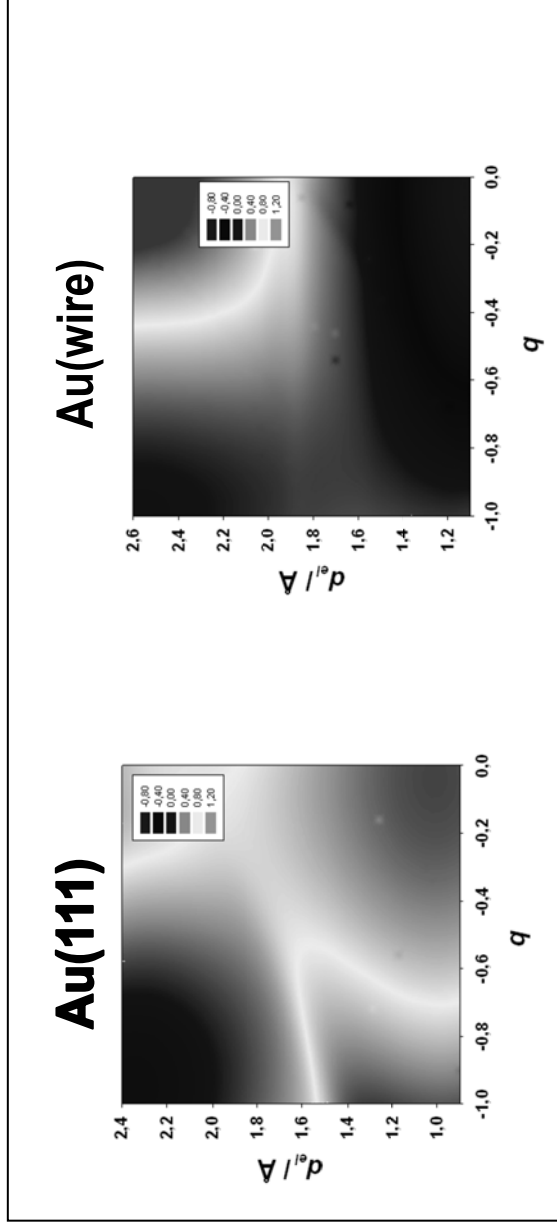


Figure 31. Contour projection of the 3D-adiabatic potential energy surfaces in thermodynamic equilibrium for the Volmer reaction as a function of the solvent coordinate  $q$  and the distance to the electrode  $d_{el}$  for a Au(111) surface and an infinite, monoatomic Au nanowire (Data obtained from Ref. 61.)

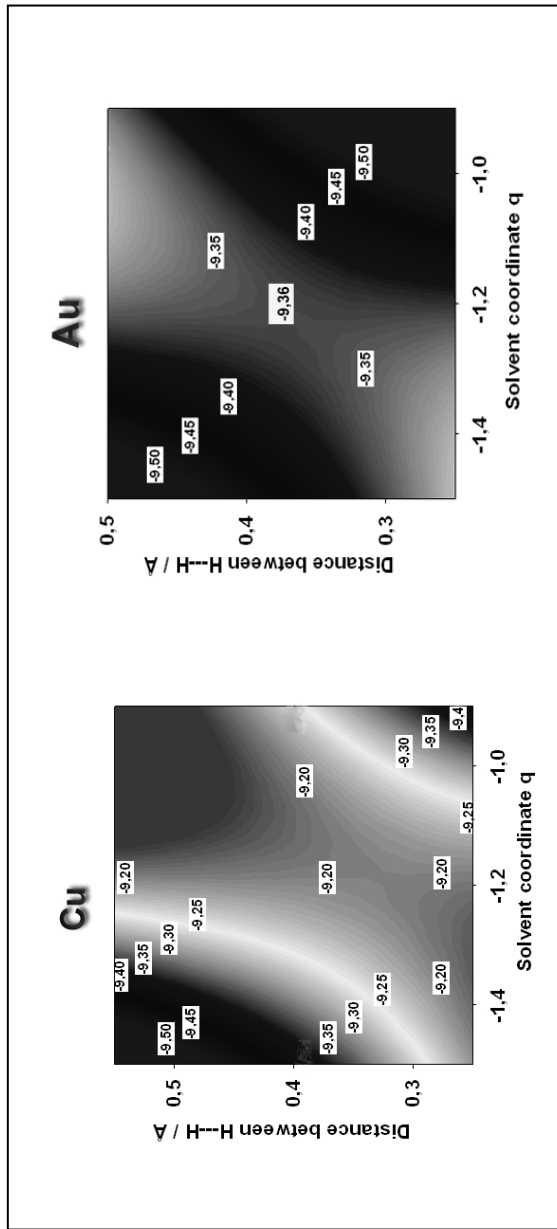


Figure 32. Contour projection of the 3D-adiabatic potential energy surfaces in thermodynamic equilibrium for the  $H_2$  overall reaction as a function of the solvent coordinate  $q$  and separation distance  $r-r_0$  between the atoms of the  $H_2$  molecule for a monolayer of Pd on Au(111) and Cu(111).

faster on a monolayer of Pd on Au(111) than on a monolayer on Cu(111) as can be observed from the contour plots of Fig. 32. A cluster of three atoms on Au(111) still shows a larger electrocatalytic activity. The last results correlate very well with experimental measurements.<sup>56</sup> However, not only the change in the structures of the *d bands* plays a role in the electrocatalytic properties. There are a series of other factors, such as the interaction with the solvent and the type of reaction. For example, in the case of a reduction reaction, there is no important differences in the electrocatalytic activity of the monolayer on Au(111) and the Pd(111) surface. This differences in the electrocatalytic effect can be understood by taking into account that the optimal position of the *d band* is different for a reduction and an oxidation reaction (see Fig. 22).

### XIII. CONCLUSIONS

For a long time the theory, and indeed the understanding, of electrochemical reactions had been limited to outer sphere electron transfer and the Marcus-Hush,<sup>10,11</sup> Levich-Dogonadze<sup>19</sup> kind of theory. The situation was so desperate that these theories were sometimes applied to reactions which were definitely not outer sphere, such as metal deposition or hydrogen evolution – with some regret; we refrain from giving a list of appropriate citations. But during the last one or two decades there has been a rapid, accelerating progress in understanding electrocatalysis.

This progress can be traced to two factors: One is, of course, the availability of DFT codes<sup>12-14</sup> combined with the ever increasing power of computers. The urgent need for better and cheaper electrocatalysts has entailed numerous DFT studies of fuel cell reactions, in particular oxygen reduction and hydrogen oxidation. Indeed, with the aid of DFT, if intelligently applied, the thermodynamics of many electrochemical reactions or reaction steps can be elucidated. However, as we pointed out in this article, DFT itself is not enough, since it cannot handle electron transfer, which involves collective solvent fluctuations. Therefore, a major development of reaction theory was required as a second factor. Its beginnings can be traced to the model for bond-breaking electron transfer initiated by Saveant,<sup>26,27</sup> which was later generalized and formalized into the SKS Hamiltonian.<sup>15,16</sup> These theories provide a

framework, for the treatment of inner-sphere electron transfer. An important step in the development of these theories was the abandonment of the wide-band approximation, which is mathematically very tempting, since in many cases it allows analytical or semi-analytical solutions. However, as its name implies, it is unsuited to describe the narrow *d bands*, which effect catalysis. For *d bands*, the simple model of semi-elliptic bands is very useful, since it reproduces and explains major features such as the formation of bonding and anti-bonding states between the valence orbital of the reactant and the metal *d band*.<sup>43-45</sup> With hindsight, it seems a little strange that this model, which dates back to the original work of Newns<sup>39</sup>, was so late to arrive in electrochemistry. Combined with Hamiltonians like SKS, this model<sup>43-45</sup> demonstrates very well what we think is the principle effect of catalysis, the dynamic broadening of the reactant's density of states as it passes the Fermi level.

For quantitative calculations, DFT and theories complement each other well. DFT can provide the electronic parameters for particular reactions, and can compensate the well-known shortcomings of Anderson-Newns<sup>34,39</sup> like Hamiltonians. The first applications of the combination of DFT with theory to the hydrogen reaction, which we have presented above, are encouraging: They explain very well the different catalytic activities of the various metals, give the correct trend and order of magnitude for the rate constants.

From a theoretical point of view, the major problem is the role of the solvent, which in the present version enters into two parameters: the energy of solvation of the reactant,<sup>49,53-55,61</sup> which enters into the overall energy balance, and the energy of reorganization, which has been estimated based on experience with simple ions. With a major calculation effort, DFT should be able to provide a better basis for the reorganization energy. However, as long as one is only interested in catalysis, the role of solvent reorganization is of lesser importance. Since water interacts weakly with catalytically active metals, the role of the solvent will be about the same on all metals, and the reactivity will be determined by electronic effects alone.

So far, our theory has been explicitly developed and applied only to the hydrogen reaction, and with good success. But even for this reaction there are many problems open, which can be tackled

with the present methods. In particular, these are cases like Pt(111), on which more than one adsorbed species exist, the Heyrowski reaction, which requires an extension of the theory, and the roles of nanostructures such as steps and overlayers. In this respect, the first results reported in Section X are quite encouraging.

The big problem is how to extend the theory and methods of electrocatalysis to other reactions. From a technological point of view, oxygen reduction is by far the most important reaction, since presently the performance of fuel cells is severely restricted by the inefficient and expensive catalysts for this reaction. At present, most of our understanding for this reaction is based on volcano-type correlations, first proposed by Trasatti,<sup>2</sup> later version by Nørskov et al.<sup>63</sup> Obviously, a proper understanding of this reaction would require a detailed investigation of the most important steps, along the line that we have applied to the hydrogen reaction. That this is no simple task can be seen from a recent paper by Vassilev and Koper,<sup>64</sup> who investigated the thermodynamics of a multitude of possible reaction steps. If one is not guided by economic necessities alone, there are other, simpler reactions, such as chloride evolution, which would be easier to investigate, and understand, within the present state of theory.

## ACKNOWLEDGEMENTS

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## REFERENCES

- <sup>1</sup> S. Trasatti, *J. Electroanal. Chem.* **39** (1972) 163.
- <sup>2</sup> S. Trasatti, *Adv. Electrochem. Electrochem. Eng. and Electrochemical Engineering*, Ed. by H. Gerischer and C.W. Tobias, Wiley, New York, Vol. 10, 1977 p. 213.
- <sup>3</sup> J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandalov, U. Stimming, *J. Electrochem. Soc.* **152** (2005) J23.

- <sup>4</sup> B. E. Conway, E. M. Beatty, P. A. D. De Maine, *Electrochim. Acta* **7** (1962) 39.
- <sup>5</sup> P. Sabatier, *Ber. Dtsch. Chem. Ges.* **44** (1984) 1911.
- <sup>6</sup> J. Horiuti and M. Polanyi, *Acta Physicochim. USSR* **2** (1935) 505; H. Gerischer, *Z. Phys. Chem.* **8** (1956) 137.
- <sup>7</sup> R. Parsons, *Trans. Farad. Soc.* **94** (1958) 1059.
- <sup>8</sup> L. Krishtalik, *Elektrokhimiya* **2** (1966) 616.
- <sup>9</sup> W. Schmickler and S. Trasatti, *J. Electrochem. Soc.* **153** (2006) L31.
- <sup>10</sup> R. A. Marcus, *J. Chem. Phys.* **24** (1965) 966.
- <sup>11</sup> N. S. Hush, *J. Chem. Phys.* **28** (1958) 962.
- <sup>12</sup> W. Kohn and L. J. Sham, *Phys. Rev.* **140** (1965) A1133.
- <sup>13</sup> J. Perdew and A. Zunger, *Phys. Rev. B* **23** (1981) 5048.
- <sup>14</sup> R. G. Parr and W. Yang, in *Density Functional Theory of Atoms and Molecules* Oxford U. Press, New York, 1989.
- <sup>15</sup> E. Santos, M. T. M. Koper, W. Schmickler, *Chem. Phys. Lett.* **419** (2006) 421.
- <sup>16</sup> E. Santos, M. T. M. Koper, W. Schmickler, *Chem. Phys.* **344** (2008) 195.
- <sup>17</sup> T. Iwasita, W. Schmickler, J. W. Schultze, *Ber. Bunsen-Ges.* **89** (1985) 138.
- <sup>18</sup> E. Santos, T. Iwasita, W. Vielstich, *Electrochim. Acta* **31** (1986) 431.
- <sup>19</sup> V. G. Levich, in *Kinetics of Reactions with Charge Transfer, in Physical Chemistry*, an Advanced Treatise, Vol. Xb, ed. by H. Eyring, D. Henderson, and W. Jost, Academic Press, New York, 1970.
- <sup>20</sup> A. Groß, in *Theoretical Surface Science – a microscopic perspective*, Springer, Berlin, 2002.
- <sup>21</sup> A. Groß, in *Adsorption at nanostructured surfaces*, Chapter 89 of Handbook of Theoretical and Computational Nanotechnology, eds. Michael Rieth and Wolfgang Schommers, American Scientific Publishers, 2006.
- <sup>22</sup> R. A. van Santen, M. Neurock, in *Molecular heterogeneous catalysis*, Wiley-VCH, Weinheim, 2006.
- <sup>23</sup> B. Hammer and J. K. Nørskov, *Adv. Catal.* **45** (2000) 71.
- <sup>24</sup> K. Fukui, *Science* **218** (1982) 747.
- <sup>25</sup> E. D. German, A. M. Kuznetsov, *J. Phys. Chem.* **98** (1994) 6120.
- <sup>26</sup> J. M. Savéant, *J. Am. Chem. Soc.* **109** (1987) 6788.
- <sup>27</sup> J. M. Savéant, *Acc. Chem. Res.* **26** (1993) 455.
- <sup>28</sup> M. T. M. Koper, G. A. Voth, *Chem. Phys. Lett.* **282** (1998) 100.
- <sup>29</sup> A. Calhoun, M. T. M. Koper, G. A. Voth, *J. Phys. Chem. B* **103** (1999) 3442.
- <sup>30</sup> A. M. Kuznetsov, I. G. Medvedev, J. Ulstrup, *Electrochem. Commun.* **2** (2000) 135.
- <sup>31</sup> D. R. Hartree, *Proc. Cambridge Philos. Soc.* **24** (1928) 328.
- <sup>32</sup> V. A. Fock, *Z. Phys.* **15** (1930) 126.
- <sup>33</sup> A. M. Kuznetsov, I. G. Medvedev, *Russ. J. Electrochem.* **39** (2003) 1107; I. G. Medvedev, *Russ. J. Electrochem.* **39** (2003) 39.
- <sup>34</sup> P. W. Anderson, *Phys. Rev.* **124** (1961) 41.
- <sup>35</sup> N. Kawakami, A. Akiji, *J. Phys. Chem. Jpn.* **51** (1982) 1143.
- <sup>36</sup> A. M. Kuznetsov, I. G. Medvedev, *Electrochem. Commun.* **9** (2007) 1624.
- <sup>37</sup> Y. Gohda, S. Schnur and A. Groß, *Faraday Discuss.* **140** (2009) 203.
- <sup>38</sup> S. G. Davison, K. W. Sulston, in *Green Function Theory of Chemisorption*, Springer-Verlag, London, in press.
- <sup>39</sup> D. M. News, *Phys. Rev.* **178** (1969) 1123.
- <sup>40</sup> W. Schmickler, *Electrochim. Acta* **21** (1976) 161.
- <sup>41</sup> W. Schmickler, *J. Electroanal. Chem.* **204** (1986) 31.
- <sup>42</sup> W. Schmickler, *Chem. Phys. Lett.* **237** (1995) 152.

- <sup>43</sup> E. Santos and W. Schmickler, *ChemPhysChem* **7** (2006) 2282.
- <sup>44</sup> E. Santos and W. Schmickler, *Chem. Phys.* **332** (2007) 39.
- <sup>45</sup> E. Santos and W. Schmickler, *Electrochim Acta* **53** (2008) 6149.
- <sup>46</sup> J. C. Slater, in *Quantum Theory of Molecules and Solids*, Addison-Wesley, Reading, Mass. 1972.
- <sup>47</sup> M. Wolfsberg and L. Helmholz, *J. Chem. Phys.* **20** (1952) 837.
- <sup>48</sup> Schmickler W. in *Interfacial Electrochemistry*, New York, Oxford University Press, 1996.
- <sup>49</sup> E. Santos and W. Schmickler, *Angew. Chem. Int. Ed.* **46** (2007) 8262.
- <sup>50</sup> J. Clavilier, R. Faure, G. Guinet, R. Durand, *J. Electroanal. Chem.* **107** (1980) 205.
- <sup>51</sup> D. Eberhard, E. Santos, W. Schmickler, *J. Electroanal. Chem.* **461** (1999) 76.
- <sup>52</sup> D. Eberhard, in *Ph.D. thesis*, University of Ulm, 1999.
- <sup>53</sup> E. Santos, K. Pötting and W. Schmickler, *Faraday Discussions* **140** (2008) 209.
- <sup>54</sup> E. Santos, A. Lundin, K. Pötting, P. Quaino and W. Schmickler, *J. Solid State Electrochemistry* **13** (2009) 1101, DOI: 10.1007/s10008-008-0702-4. (on line).
- <sup>55</sup> E. Santos, A. Lundin, K. Pötting, P. Quaino and W. Schmickler *Physical Review B* **79** (2009) 235436.
- <sup>56</sup> See e.g. S. Pandelov, and U. Stimming, *Electrochim. Acta* **52** (2007) 5548, and references therein.
- <sup>57</sup> F. Hernandez and H. Baltruschat, *J. Solid State Electrochem.* **11** (2007) 877.
- <sup>58</sup> H. Baltruschat, R. Bušar, S. Ernst and F. Hernandez, in: *In-situ Spectroscopic Studies of Adsorption at the Electrode and Electrocatalysis* Paul A. Christensen, Andrzej Wieckowski and Shi-Gang Sun (eds), Elsevier, 2007.
- <sup>59</sup> R.R. Adzic, A.V. Tripkovic, and V.B. Vessovic, *J. Electroanal. Chem.* **204** (1986) 329.
- <sup>60</sup> G. Garcia and M.T.M. Koper, *Phys. Chem. Chem. Phys.* **10** (2008) 3802.
- <sup>61</sup> E. Santos, P. Quaino, G. Soldano, and W. Schmickler, *Electrochem. Comm.* **11** (2009) 1764.
- <sup>62</sup> E. Leiva, P. Vélez, C. Sanchez, and W. Schmickler, *Phys. Rev. B* **74** (2006) 035422.
- <sup>63</sup> J.K. Norskov et al., *J. Phys. Chem. B* **108** (2004) 17886.
- <sup>64</sup> P. Vassilev and M.T.M. Koper, *J. Phys. Chem. C* **111** (2007) 2607.

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