

Hydrogen evolution reaction on palladium multilayers deposited on

Au(111): a theoretical approach.

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Supporting Information

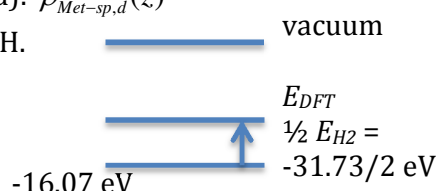
Theory of Electrocatalysis for the Volmer reaction [1-4]: $\text{H}^+ + \text{e}^- \rightarrow \text{H}_{\text{ads}}$

The proton approaches to the surface from the bulk of the solution. ('distance' coordinate, z). There are fluctuations of the solvent configuration described by the 'solvent' coordinate, q .

When a H-atom approaches to the surface, we obtain from DFT:

- the density of states projected onto the 1s orbital of the hydrogen atom for the absence of solvent: $\rho_H(z, q=0)$
- the density of states projected onto the electronic states of the metallic atoms of the surface (sp-band and d-band): $\rho_{\text{Met-sp,d}}(z)$
- the energy, using as reference: $\frac{1}{2} \text{H}_2 \rightarrow \text{H}$.

Adding the entropy correction $-T \Delta S = -0.41 \text{ eV}$:



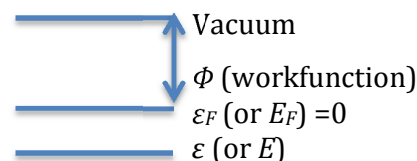
Therefore, we add 0.2 eV to the values obtained by DFT:

$$E_{\text{DFT}} + 0.2 \text{ eV}$$

According to Anderson -Newns [5-6], the density of states corresponding to the 1s orbital of the H-atom interacting with the metal and the solvent is:

$$\rho_H(\varepsilon) = \frac{1}{\pi} \frac{\Delta(\varepsilon)}{[\varepsilon - (\varepsilon_H + \Lambda(\varepsilon) - 2\lambda q)]^2 + \Delta(\varepsilon)^2}$$

the reference point for the energy is the Fermi level:



ε_H is the position of the center of ρ_H . When the H-atom is far away from the surface, it is the energy level of the orbital 1s.

The chemisorption functions $\Delta(\varepsilon)$ and $\Lambda(\varepsilon)$, produce a broadening and a shift of the electronic states of the H-atom, respectively, and are given by:

$$\Delta(\varepsilon) = \sum_k |V|^2 \pi \delta(\varepsilon - \varepsilon_k) \approx |V|^2 \pi \rho_{Met}(\varepsilon) = \Delta_{sp}(\varepsilon) + \Delta_d(\varepsilon) = |V_{sp}|^2 \pi \rho_{Met-sp}(\varepsilon) + |V_d|^2 \pi \rho_{Met-d}(\varepsilon)$$

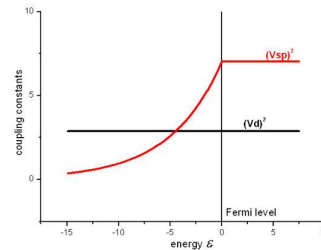
$$\Lambda(\varepsilon) = \frac{1}{\pi} P \int \frac{\Delta(\varepsilon')}{\varepsilon - \varepsilon'} d\varepsilon' = \Lambda_{sp}(\varepsilon) + \Lambda_d(\varepsilon)$$

where $|V_{sp}|^2$ and $|V_d|^2$ are the coupling constants of the H-atom with the sp and d band, respectively (overlap interaction integrals: $\langle k|V|H \rangle$).

Better results were obtained if the coupling constants are assumed to have an exponential dependence with the energy below the Fermi level instead to be constants:

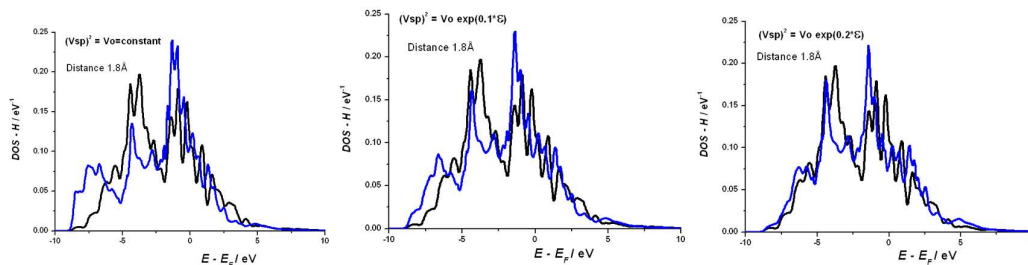
$$|V_{sp}|^2 = V_0 \exp(a \varepsilon) \quad \varepsilon < 0$$

$$|V_{sp}|^2 = V_0 = \text{constant}$$



This effect is particularly significant for the sp-band, which is much broader than the d-band.

Examples of fitting with different coupling parameters for H/Au(111) at a distance of 1.8 Å (black lines DOS obtained from DFT, blue lines DOS obtained by fitting with Anderson-Newns):



The interactions with the solvent is given by terms containing the energy of reorganization λ according to Marcus – Hush theory [7-8], and the effective normalized solvent coordinate q for the classical phonon modes (it implies an average over all but one solvent degrees of freedom). When the configuration of the slow solvent modes is characterized by a certain value q , it would be in equilibrium with a charge of $-q$ on the reactant (in our case: $q=0$, neutral H-atom; $q=-1$, proton).

Fortunately, the exact value of λ is not so important since there is a partial cancellation. When we use a model with a constant energy of reorganization λ , its exact value has only a small effect, as long as it is within a reasonable range, according to our estimates.

We used a simple interpolation between surface and bulk values:

$$\lambda(\text{distance}) = \lambda_{\infty} p(z/L); \quad p(x) = \begin{cases} 0 & \text{for } x < 0 \\ (3-2x)x^2 & \text{for } 0 \leq x \leq 1 \\ 1 & \text{for } 1 < x \end{cases}$$

where λ_{∞} is the value in the bulk, which falls off by a factor of 2 over a distance of $L=3\text{\AA}$. The interpolating polynomial has been chosen such that it interpolates over the two limiting values with zero gradient at the end point. In our model calculations, we have used both a variable and a constant value of λ to explore the consequences [4].

Therefore, the total energy of the H-atom and the solvent is:

$$E(q) = \int_{-\infty}^{\varepsilon_F=0} \rho_H(\varepsilon) \varepsilon d\varepsilon + \lambda q^2 + 2\lambda q$$

In order to correct the value to the same reference that the Energy obtained by DFT, we have to subtract the work function and $\frac{1}{2} E_{H2}$. We shall call it 'Anderson - Newns Energy, EAN':

$$EAN(q) = E(q) - \Phi + 16.05$$

We use the DFT Energy for the correction due to missing terms corresponding to the correlation and Exchange. We take EAN for $q=0$:

$$\Delta E(q) = \Delta E(q=0) * \text{occupation} = (EAN(q=0) - E_{DFT}) * \int_{-\infty}^{\varepsilon_F=0} \rho_H d\varepsilon$$

Then:

$$E_{\text{tot}} = EAN(q) - \Delta E(q)$$

In the case of equilibrium between the proton and the H-atom:

$H^+ + e^- = H$ $\eta=0$ and $E(q=-1)=0$; and the energy for the proton should be the reorganization energy of the solvent λ . Therefore, we have to add an extra correction term to EAN:

$$\text{proton} = (1 - \int_{-\infty}^{\varepsilon_F=0} \rho_H d\varepsilon) (-\Phi + 16.05 - \lambda).$$

$$E_{\text{final}} = E_{\text{tot}} - \text{proton} = (E(q) - \Phi + 16.05) - \Delta E(q) - \text{proton} =$$

$$E_{\text{final}} = \left[\int_{-\infty}^{\varepsilon_F=0} \rho_H(\varepsilon) \varepsilon d\varepsilon \right] + \lambda q^2 + 2\lambda q - \Phi + 16.05 - \left\{ \left[\int_{-\infty}^{\varepsilon_F=0} \rho_H(\varepsilon) \varepsilon d\varepsilon \right]_{q=0} - \Phi + 16.05 - E_{DFT} \right\} \int_{-\infty}^{\varepsilon_F=0} \rho_H(\varepsilon) d\varepsilon - \left[1 - \int_{-\infty}^{\varepsilon_F=0} \rho_H(\varepsilon) d\varepsilon \right] (-\Phi + 16.05 - \lambda)$$

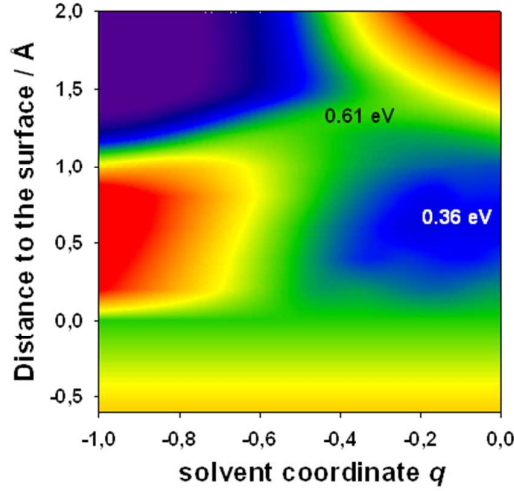
According to these definitions, when $q=0$, $\text{occu}=1$, (H-atom)

$$E_{\text{final}} = E_{DFT}$$

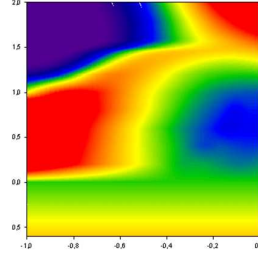
When $q=-1$, $\text{occu}=0$ (proton H^+)

$$E_{\text{final}} = 0$$

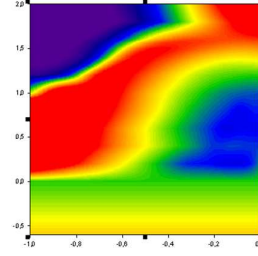
Energy Surfaces obtained with the different coupling parameters for H/Au(111):
 $IV_{sp}I^2 = V_0 \exp(0.2 * \varepsilon)$



$IV_{sp}I^2 = V_0 \exp(0.1 * \varepsilon)$



$IV_{sp}I^2 = V_0 = \text{constant}$



There is an overestimation of the activation barrier when the fit is carried out without enough precision in the DOS.

Computational details

First-Principles Calculations

All calculations were performed using the dacapo code [9]. This utilizes an iterative scheme to solve the Kohn-Sham equations of density-functional theory selfconsistently. A plane-wave basis set is used to expand the electronic wave functions, and the inner electrons were represented by ultrasoft pseudopotentials [10], which allow the use of a low-energy cutoff for the plane-wave basis set. An energy cutoff of 450 eV, dictated by the pseudopotential of each metal, was used in all calculations. The electron-electron exchange and correlation interactions are treated with the generalized gradient approximation in the version of Perdew et al. [11]. The Brillouin-zone integration was performed using a $8 \times 8 \times 1$ k-point Monkhorst-Pack grid [12] corresponding to the 1×1 surface unit cell. Spin-polarization was only considered when the hydrogen atom was farther than 2.2 Å from the surface where

the systems become spin polarized otherwise no magnetic effects were evaluated. Dipole correction was used to avoid slab-slab interactions.

Modeling

To study the hydrogen adsorption/absorption processes, several systems were considered: a pure metal surface -Pd(111) and Au(111)- and overlayers of Pdn (n=1,2) deposited on Au(111). The clean surfaces were modelled by a (2×2) supercell with 4 metal layers. For the alloy a (2×2) supercell with 3 substrate-layers -Au(111)- and n (n=1,2) adatom-overlayer(s) were used. In all the calculations 10 layers of vacuum were considered. For all the systems, the two bottom layers were fixed at the next-neighbor distance corresponding to bulk and all the other layers were allowed to fully relax. The convergence criterion was achieved when the total forces were less than 0.02 eV/Å. The theoretical lattice parameters for each metal were obtained from the calculated equilibrium distances of a periodic fcc bulk, optimized values are the following: $a_0^{\text{Pd}}=3.99$ Å and $a_0^{\text{Au}}=4.18$ Å. Within the typical statistical errors, both constants are in agreement with the experimental values ($a_0^{\text{Pd}}=3.89$ Å and $a_0^{\text{Au}}=4.08$ Å) reported in the literature.

To mimic the adsorption/penetration/absorption processes and evaluate their barriers, we performed a series of calculations for a single atom adsorbed on a fcc-hollow site (equilibrium position), and varied its separation from the surface into the vacuum (adsorption/desorption). For the case of the absorption phenomena, the minimum energy path from the surface to the first subsurface position was from the fcc-hollow site to the octahedral site underneath (as in most (111) facets). The octahedral site was evaluated between the first and the second metal layers, and it corresponds to the threefold site that has a metal atom directly below in the third layer showing a coordination number of 6. The H-atom was kept fixed at different z-distances

perpendicular to the surface and allowed to relax in the xy coordinates during these calculations. At each position the corresponding energy (adsorption or absorption energy) and the density of states projected onto different atoms have been calculated (1s-H, 4sp-Pd, 4d-Pd, 6sp-Au, 5d-Au). A coverage of 0.25 monolayers (ML) of H was considered for both adsorption and absorption. According to the absorption possibilities, there also exists a tetrahedral absorption site, which corresponds to the threefold site that has a metal atom directly below in the second layer with a coordination number of 4; but since the typical penetration path proceeds from the fcc-hollow site to the octahedral subsurface site in the (111) facets, this process was not evaluated in the tetrahedral environment. However, for the sake of completeness, the energetics of palladium overlayers (n=2,3,4) for a full monolayer of hydrogen have been investigated in both environments, tetrahedral and octahedral, and compared them with bulk palladium.

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