

Solvated protons in density functional theory—A few examples



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ABSTRACT

We have investigated several ways of introducing a solvated proton into a DFT calculation in order to mimic an electrochemical interface: an extra hydrogen introduced into a metal bilayer, a Zundel and an Eigen ion. In all these cases the charge on the supposed proton is substantially less than a unit positive charge. In contrast, when the electrode is represented as a cluster, the charge on Zundel ion is indeed plus one. However, the distribution of the compensating charge on the cluster is quite different from that on a plane metal surface.

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1. Introduction

During the last decade, much effort has been spent in modeling electrochemical interfaces with density functional theory (DFT). One of the principal difficulties is to incorporate charge separation between the two phases, and this implies that the solvent part of the interface must contain ions. When DFT is used in the periodic slab configuration, it is not straightforward to put ions into the system. DFT minimizes the energy of the system, and places the electrons wherever it is energetically most favorable. If there is sufficient solvent in the system, ions that are stable in water should form spontaneously, as can be seen by going through a simple Born–Haber cycle. Let us take the proton, on which this article is focused, as an example. A single hydrogen atom placed in water does not interact strongly with its surroundings. Taking an electron away costs about 13.6 eV, but the gain in solvation energy is -11.3 eV; placing the electron onto the electrode entails on energy gain given by the work function, which for metals are of the order of 4–5 eV. Thus the formation of the proton is favorable when the hydrogen is not adsorbed on the electrode. However, this argument holds only if the solvation of the proton in the model system is sufficiently strong. Also, this argument ignores the electric field that is formed at the interface when the electron

is transferred to the metal, and which also stores energy. In real systems this field will be shielded by the reorientation of water, but in the model this can only happen if there is sufficient water.

However, an advice like: ‘use sufficient water’ is not really useful, since adding water molecules is computationally expensive. Therefore, we examine here the charge on the proton in a few common configurations: an extra hydrogen atom added to a water bilayer on Pt(1 1 1), a Zundel ion H_5O_2^+ and an Eigen ion H_9O_4^+ on Au and Pt surfaces, both in the absence and in the presence of an external field. Finally, we consider the situation for a Zundel ion in front of a metal cluster calculated by the Gaussian program, which does not use the slab configuration, and allows to place charges onto atoms. The technical details for the reported calculations have been relegated to Appendix A.

2. Proton in a water bilayer on Pt(1 1 1)

In the vacuum, water adsorbs on Pt(1 1 1) at low temperatures and forms a water bilayer, whose structure is well-documented in the literature [1]. Therefore, a metal slab in contact with one or more bilayers of water has become quite a popular model for the electrochemical interface [2], and the group of Nørskov et al. [3] have charged this interface by adding extra hydrogen atoms to the bilayer, which acquired a positive charge. In order to investigate the charge separation in models of the electrochemical interface based on the water bilayer, we have investigated the following situation:

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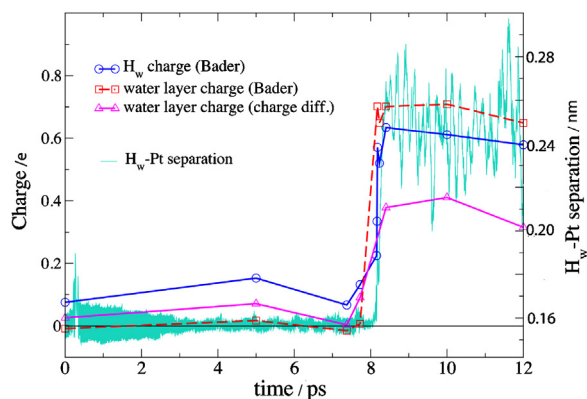


Fig. 1. Position and positive charge on the extra hydrogen atom H_w and charge on the water layer over the course of the molecular dynamics run.

hydrogen atoms adsorb strongly on platinum, and in the potential region where hydrogen evolution takes place, the Pt(1 1 1) surface is already covered by hydrogen atoms strongly adsorbed in the fcc(1 1 1) hollow sites. We have therefore considered a Pt(1 1 1) surface covered with a monolayer of this strongly adsorbed hydrogen H_s – in the electrochemical literature this hydrogen is also known as upd hydrogen, i.e. hydrogen deposited at underpotential – and by two layers of water within the familiar $2\sqrt{3} \times 2\sqrt{3}R30^\circ$ geometry. This structure was allowed to relax at zero Kelvin. To this system we added a single hydrogen atom adsorbed on a top site, which is the next favorable site. The corresponding adsorbed hydrogen is known as weakly adsorbed hydrogen H_w , or opd hydrogen (adsorbed at overpotentials). This setup was used as the starting configuration in an ab initio molecular dynamics (AIMD) simulation performed at room temperature; the technical details have been published in Ref. [4].

The motion of the weakly adsorbed hydrogen and the concomitant changes in charge distribution, obtained from Bader analysis, are shown in Fig. 1. At short times, a slight rearrangement of the hydrogen atoms, which are the lightest particles, takes place. The adsorbed hydrogen atoms repel each other, and the strongly adsorbed hydrogen atoms move a little away from the fcc hollow sites [5]. The average position of the H_w atom at first does not change much, till suddenly, after about 8.2 ps, it jumps into the water layer, where it becomes solvated. Obviously, this jump requires a favorable fluctuation in the water, which has to assume a configuration that is suitable to accept another hydrogen atom. Note the large fluctuations in the position of the extra hydrogen after it has jumped to the water layer. Qualitatively similar behavior of the charge distribution of a solvated proton on a mercury surface vs. the proton–metal distance was reported previously in Ref. [6] on the basis of cluster calculations

For our purpose, the development of the charge on the extra H_w atom is of particular interest. In the initial state, its positive charge is quite small, of the order of 0.1 units. After it has jumped to the water layer, its charge becomes more positive, of the order of 0.6 units; evaluation of charge differences gives a somewhat smaller value of about 0.4 units. Actually, the charge on an atom is not an observable and depends on the attribution of the electronic density to individual atoms. Therefore, different methods tend to give somewhat different values. The important point is that the excess charge is somewhere intermediate between zero and unity. The hydrogen atoms pertaining to water molecules also carry a positive charge of about the same magnitude, indicating that all hydrogen atoms within the layer are equivalent, like one would expect to happen in the long run. When the excess hydrogen jumps into the water layer the total charge in that layer, which now includes the extra hydrogen, also rises. The increase in the total charge of the water layer

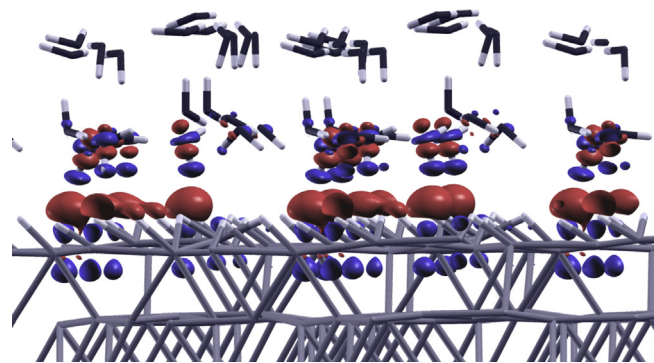


Fig. 2. Distribution of the excess charge after 10 ps. Red indicates electron buildup.

is somewhat larger than that on the extra hydrogen, indicating a certain delocalization of the positive charge.

The excess positive charge within the water layer must be balanced by a negative excess charge concentrated on the metal surface. In order to investigate in detail the charge distribution we have calculated the electron density differences for $t > 8.20$ ps, i.e. after the jump, according to: $\Delta\rho(\mathbf{r}) = \rho_{\text{full}}(\mathbf{r}) - [\rho_{\text{Pt}+H_s}(\mathbf{r}) + \rho_{H_{sw}+H_2O_b}(\mathbf{r})]$, where $\rho_{\text{Pt}+H_s}(\mathbf{r})$ is the electron density distribution of the H-covered Pt surface, and $\rho_{H_{sw}+H_2O_b}(\mathbf{r})$ is the electron density distribution of the water bilayers with the extra hydrogen. Fig. 2 shows the situation after 10 ps. It clearly shows an excess negative charge located mainly on the H_s atoms, between the metal surface and the water layer, which in a classical context would be an image charge, i.e. the surface charge which mimics an image inside the metal.

3. Zundel and Eigen ion

In water at ambient temperatures, there are two stable forms of the solvated proton: the Zundel ion $H_5O_2^+$ and the Eigen ion $H_9O_4^+$. In the vacuum the Zundel ion has almost C_{2v} geometry, when it is adsorbed on a metal surface it lies flat. The energy of ionization of the neutral molecule H_2O_2 is about 4.36 eV. Therefore, at a first glance one should expect a transfer of an electron to metals with work functions larger than this value. However, this simple consideration disregards the fact, that DFT can place partial charges onto atoms even if they do not participate in a chemical bond; in addition, as mentioned before, an ion in front of a metal surface generates an electric field, which also contains energy.

We have studied the adsorption of the Zundel molecule H_5O_2 on several surfaces – by calling it a molecule we anticipate that it carries little excess charge. Typical configurations for the adsorption on (1 1 1) surfaces are shown in Fig. 3. The corresponding energies of adsorption are given in Table 1. Considering the fact that water adsorbs but weakly on metal surfaces, the adsorption energies for the Zundel species are surprisingly large, indicating a chemical bond formation. They are of the same order of magnitude as the adsorption energies for a single hydrogen atom. Adsorption on the more open Au(1 0 0) surface is notably stronger than on the others. For Pt(1 1 1) and Ag(1 1 1) we have varied the surface coverage by changing the size of the unit cell. The adsorption energies

Table 1

Adsorption energies of the Zundel molecule on various substrates and for various sizes of the unit cell; all energies are in eV.

Au(1 0 0)	Au(1 1 1)	Pt(1 1 1)		Ag(1 1 1)	
3×3	3×3	3×3	4×4	3×3	4×4
-3.52	-2.29	-3.04	-3.49	-1.97	-2.29

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