



## Avoiding pitfalls in the modeling of electrochemical interfaces

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### ABSTRACT

Alignment of metal and molecular electronic energy levels at electrode–electrolyte interfaces is investigated using density functional theory. Three different regimes exhibiting qualitatively different energy level alignments are observed. The regimes are roughly defined by the size of the metal work function relative to the ionization potential and/or electron affinity of the electrolyte. It is demonstrated that proper matching of these quantities is essential for successful *ab initio* modeling of electrochemical interfaces and it is further discussed how such matching can be obtained by careful tailoring of the interfacial atomic structure.

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Electrochemical cells have a unique capability to perform efficient conversions between free energy stored in chemical fuels and potential differences, which can be transformed into electrical work [1]. The energy conversion occurs through charge transfer reactions taking place over the electrochemical interface, the border region separating the electron-conducting electrode and the electrically insulating but ion-conducting electrolyte. The efficiency of conversion is, to a great extent, determined by the energetics of single charge transfer reactions. Therefore, it is of utmost importance to gain an atomic-level understanding of the electrochemical interface.

In the last decade, density functional theory (DFT) based atomic and electronic structure simulations of electrochemical interfaces have emerged [2–14]. The objective of these simulations is to study charge transfer reactions and electrochemical properties that usually depend on the electrode potential. Hence, a scheme for assessing the potential is indispensable. Most commonly, the work function, evaluated in vacuum outside the electrolyte, is used as a measure of the electrode potential [3,11,15,16].

The DFT methods have indeed proven valuable and promising in providing atomic level descriptions of various properties of the electrochemical interface [4,7,9,11,17]. In this Letter, however, we address a critical issue regarding the electronic structure of the interface, the alignment of metal and molecular electronic energy levels [18], that so far, with a few notable exceptions [12,14,19], has been largely overlooked in *ab initio* electrochemical modeling. We demonstrate that the HOMO and LUMO levels of the isolated electrolyte have to straddle the Fermi level of the metal electrode in order for the combined system to qualify as an adequate model of the electrochemical interface. In particular, we show that when

the work function of the bare metal falls outside the HOMO–LUMO range, the interface becomes conductive and charge is transferred between the originally neutral electrode and electrolyte. For such systems it is not possible to model changes in the electrode potential. Although a conductive interface might sometimes be a true physical effect, it is often a consequence of the unphysical self-interaction experienced by electrons in conventional DFT, which introduces errors in calculated electron affinities and ionization potentials. Spurious interfacial charge transfer has implications beyond the field of electrochemical interface modeling. For instance, it will give an additional contribution to work functions calculated for metal–water systems, thus making comparisons between experimental and theoretical structures ambiguous. Finally, aside from pointing out the pitfalls faced when modeling electrochemical interfaces, we also describe how they can be avoided by controlling the atomic configuration and the corresponding electronic structure.

Most of the DFT calculations are performed at the GGA–RPBE [20] level of exchange–correlation, using DACAPO [21], a plane-wave Vanderbilt ultrasoft pseudopotential [22] code. Metal lattice constants are optimized at the RPBE level and are then used in all calculations. Interfaces are modeled by periodically repeated  $3 \times 2$  unit cells wide and 3 layer thick metal slabs with an electrolyte film adsorbed on top. Periodic images are separated by at least 12 Å of vacuum in the direction perpendicular to the metal surface, a setup that ensures convergence of work functions and energies. When applicable, the dipole correction is used to decouple the electrostatic interaction between periodically repeated slabs [23]. The Kohn–Sham equations are solved using a plane-wave cutoff of 26 Ry, and the k-points are sampled using a  $4 \times 6 \times 1$  Monkhorst–Pack k-point grid [24]. In addition, some GGA + U calculations [25] are carried out using GPAW [26,27], a real-space projector-augmented wave (PAW) [28] code, with a grid spacing of about 0.18 Å.

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Figure 1 shows an example of an electrochemical metal–water interface. The surface charge density and hence the electrode potential can be varied either by injecting (removing) electrons into (from) the metal slab [3] or by adding hydrogen atoms to the first water layer [6,11]. In the former case the additional negative (positive) charge is compensated by a background charge of opposite sign to ensure overall charge neutrality of the computational cell. In the latter case, the additional hydrogen atoms spontaneously separate into protons that become solvated in the water bilayer and electrons that end up on the surface of the metal slab. Again the computational cell remains charge neutral. In the example shown in Figure 1 the latter approach has been adopted. The electrostatic potential (EP) energy has been plotted for two different proton concentrations. It is seen that an increase in proton concentration, and concomitant increase in surface charge density, reduces the EP energy in the vacuum region outside the electrolyte, relative to the Fermi level; that is, it reduces the work function  $\Phi'$  which is a measure of the electrode potential [3,15,16]. This interface model thus allows the bias to be varied and electrochemical reactions to be studied at different potentials.

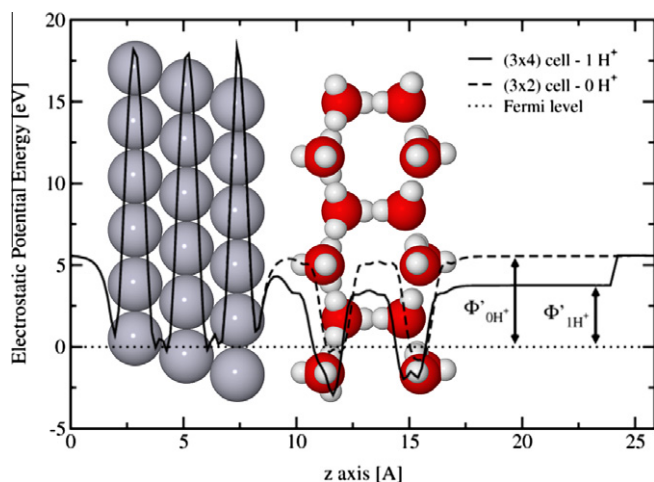
The explanation as to why  $\Phi'$  can be varied in the above system is found in the relative size of the metal work function,  $\Phi_M$ , compared to the electron affinity,  $E_A$ , and ionization potential,  $E_I$ , of the electrolyte. Based on the relative size, the so-called integer charge transfer model [29], applicable to interfaces with weak interaction between electrodes and electrolytes, identifies three different regimes, each with a unique alignment of metal and molecular electronic energy levels. More precisely, the three regimes (or regions) are defined by  $\Phi_M \lesssim E_A$  (region I),  $E_A \lesssim \Phi_M \lesssim E_I$  (region II), and  $\Phi_M \gtrsim E_I$  (region III). For a comprehensive discussion of the alignment of electronic levels in these regimes the reader is referred to Refs. [18,29]. Here we will introduce only the bare minimum of quantities and concepts needed for the ensuing discussion.

The model interface displayed in Figure 1 belongs to region II. Since  $\Phi_M > E_A$  for this interface, the energy cost of removing an electron from the metal is larger than the energy gained by adding it to the electrolyte. Likewise, since  $E_I > \Phi_M$ , the cost of removing an electron from the electrolyte will not be compensated by the energy gained when adding it to the metal. Consequently, there will be no spontaneous charge transfer across the interface when

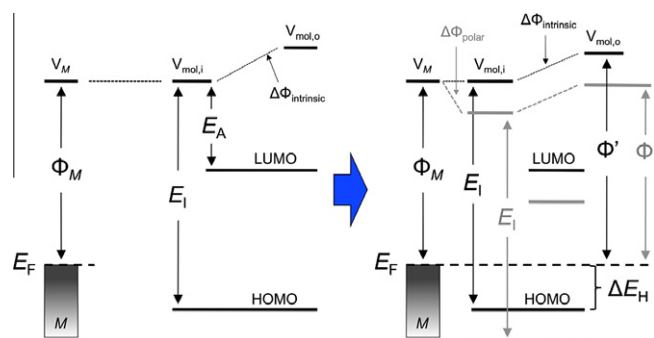
the metal and electrolyte are brought into contact to form the interface. It also means that no additional dipole will build up at the interface and the metal and electrolyte vacuum levels will therefore stay aligned upon formation of the interface, as illustrated in Figure 2. As a direct result of the vacuum level alignment, the electrolyte HOMO and LUMO levels straddle the Fermi level in the combined system.

A subsequent increase or reduction of the charge density on the metal surface – for instance in response to an applied electrode potential – adds an extra contribution,  $\Delta\Phi_{\text{polar}}$ , to the surface dipole energy, which shifts the electronic energy levels of the electrolyte relative to the Fermi level (cf. gray lines in Figure 2). This shift should be reflected in a corresponding change of  $\Phi'$  (also indicated in Figure 2), something that can be verified and quantified by DFT calculations. Figure 3b demonstrates the response of  $\Phi'$  to a change in surface charge density for another system belonging to region II, a Pt(111) surface covered with a single water bilayer with hydrogen pointing down. Here, in contrast to the example shown in Figure 1, a change in surface charge density is obtained by explicit injection of fractional charges into the metal slab. As expected,  $\Phi'$  depends sensitively on the surface charge density. Addition of 0.5 electrons to the uncharged cell with 12 surface atoms reduces  $\Phi'$  with approximately 1 eV, and addition of another half electron reduces it 1 eV further.

In systems belonging to region I, the metal donates electrons to the LUMO level of the electrolyte when the interface is being formed. After equilibrium has been established, the Fermi level will therefore be pinned to states close to the LUMO. Consequently, a change in surface charge density will not affect  $\Phi'$  much; it stays essentially fixed as it will be given roughly by the constant difference between the LUMO and  $V_{\text{mol},o}$ , the near-field vacuum level outside the electrolyte. This kind of energy alignment is observed for (111)-terminated Li artificially constrained to the fcc structure, with a two bilayer thick hydrogen-pointing-up water film adsorbed on top (see Figure 3a). Upon charging,  $\Phi'$  is found to decrease somewhat due to slightly increased occupation of the LUMO in the combined system. We note that although this example gives a clear illustration of the typical Fermi level pinning in region I, the system is fairly unrealistic; this particular interface is expected to be highly unstable since Li reacts with water. A more relevant example would probably be a metal–oxide contact. DFT's tendency to place LUMO levels too far below the vacuum level could easily result in pinning to LUMO-derived states even in systems where this is not supposed to occur.



**Figure 1.** Atomic-scale model of a Pt–water interface, showing the variation of the electrostatic potential (EP) energy averaged parallel to the surface. The EP energy is reported for two different surface charge densities corresponding to two different electrode potentials. The work functions  $\Phi'_{\text{IH}^+}$  and  $\Phi'_{\text{OH}^+}$  measure the absolute value of the EP energy in the vacuum region outside the electrolyte, relative to the Fermi level, for an electrolyte with and without explicit counterions in the outer Helmholtz layer.



**Figure 2.** Alignment of metal and molecular energy levels upon formation of an interface characterized by  $E_A \lesssim \Phi_M \lesssim E_I$ . Isolated systems are shown on the left side and the combined metal–electrolyte system on the right. The near-field vacuum level on the inner side of the electrolyte,  $V_{\text{mol},i}$ , differs from the level on the outer side,  $V_{\text{mol},o}$ , if the molecule possesses an intrinsic dipole moment,  $\Delta\Phi_{\text{intrinsic}}$ . The gray lines indicate the shift of molecular levels in response to a change in surface charge density. The HOMO offset  $\Delta E_H$  as well as the work function  $\Phi'$  of the combined system change accordingly.

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