ChemElectroChem

Research Article
doi.org/10.1002/celc.202300230

Chemistry Europe
European Chemical Societies Publishing

www.chemelectrochem.org

Why DFT-Based Tight Binding Gives a Better Representation of the Potential at Metal-Solution Interfaces than DFT Does

Paola Quaino,[a] José Luis Nuñez,[a] Bálint Aradi,[c] Tammo van der Heide,[c] Elizabeth Santos,[b] and Wolfgang Schmickler*[b]

In modelling electrochemical interfaces it is important to treat electrode and electrolyte at the same level of theory. Density functional theory, which is usually the method of choice, suffers from a distinct disadvantage: The inner potential is calculated as the average of the total electrostatic potential. This includes the highly localized potential generated from the nuclei. The resulting inner potential is far too high, of the order of 3.5 V, and not relevant for electrochemistry. In the density functional based tight binding (DFTB) method the electrostatic potential is much smoother, as it stems from atomic charge fluctuations with respect to neutral reference atoms. The resulting values for the electrochemical inner potential are much lower and compare well with those obtained by other, elaborate methods. Thus DFTB recommends itself as a method for treating the electrochemical interface including the inner potential.

Introduction

Density functional theory (DFT) is based on ingenious approximations to an unknown functional, and has become an invaluable tool for the investigation of surfaces and interfaces. DFT-based tight binding (DFTB)[1] is an ingenious approximation to DFT, in which many interactions have been parameterized. This makes DFTB much faster, and therefore allows calculations for larger systems or, in the case of simulations, much longer times. From a logical point of view, DFTB should be less exact than DFT, and inherit its weak points. That it should be in some respects better at treating metal-solution interfaces, must be due to special circumstances, and indeed it is. It has to do with the problem of the inner potential in electrochemistry, which in textbooks is defined as the work required to take a unit test charge from infinity outside the phase to a point inside.[2,3] This definition is quite useless; the electrostatic potential inside a phase is not constant, but depends on the position. In the case of an aqueous solution it is lower near an oxygen atom, higher near hydrogen, and diverges at the position of an atomic nucleus. Nevertheless, it is an important concept in electrochemistry, since differences in the inner potential between two phases of equal composition can be measured, and this is the way in which electrode potentials are determined.

Two of us have recently discussed the meaning of the inner potential[4] and the difficulties associated with this concept in an educational article. In electrochemistry the inner potential ϕ of an electrolyte solution is best defined through the electrochemical potential of an ion: $\tilde{\mu}=\mu+ze_0\phi$, where μ is the chemical part, ϕ determines the electrostatic part, and z is the charge number. $\tilde{\mu}$ is measurable, at equilibrium it is constant within a phase, and if the reference point is chosen just outside an aqueous solution it coincides with the real free energy of hydration. The problem lies with the division of the electrochemical potential into a chemical and an electrostatic part. It is not clear if all ions experience the same inner potential ϕ, which must correspond to an average electrostatic potential in voids between the water, resp. the solvent, molecules. When the reference point for the inner potential is chosen just outside the solution, the inner potential equals the surface potential, and we shall follow this convention. Based on experimental results, De Battisti and Trasatti[5] estimated a value of -0.13 V for the surface potential of water, and give references to earlier estimates based on various arguments.

In physics, a more natural concept of the inner potential is used, it is simply the average electrostatic potential inside the phase, and can be measured by high electron energy scattering. Due to its strong localization, its divergence at the positions of the nuclei, the positive charge dominates and results in average potentials of the order of several V.[6] Experimental values for ice or water lie between 3.5 V[7,8] and 4.5 V.[9] Even though in DFT the positive charge is a little smeared to avoid the divergence, it still results in high positive values close to the experimental ones – a summary has given by Yesibolati et al.[9] Therefore, high quality DFT calculations for the interface between a metal and water show a large potential drop of 3 V or more in the

[a] Prof. Dr. P. Quaino, J. L. Nuñez
Instituto de Química Aplicada del Litoral (CONICET-UNL, FIQ)
Universidad Nacional del Litoral, Santa Fe, Argentina

[b] Prof. Dr. E. Santos, Prof. Dr. W. Schmickler
Institute of Theoretical Chemistry,
Ulm University, 89069 Ulm, Germany
E-mail: wolfgang.schmickler@uni-ulm.de

[c] Prof. Dr. B. Aradi, T. van der Heide
Bremen Center for Computational Materials Science,
University of Bremen, Bremen, Germany

Research Article
doi.org/10.1002/celc.202300230

electrostatic electronic energy at the interface.[10,11] Obviously, these high values are not compatible with electrochemical experience; amongst others they would imply large differences in the free energies of anions and cations.

In a realistic calculation of the inner potential the divergence of the positive charge must be compensated. In this respect force fields models do a much better job: The partial charges on the oxygen and the hydrogen atoms of water are represented as point charges, so that all the divergences compensate each other. The values obtained depend on the water model, and vary in the range between -0.48 V and -0.89 V.[12] In DFTB the electrostatic potential is calculated from atomic charge fluctuations with respect to neutral atoms. In a homogeneous material, where there is no net charge transfer between the atoms, the resulting electrostatic potential is zero. Consequently, the electrostatic potential in DFTB does not contain the singular potential of the nuclei, which is screened by the electrons in a neutral atom. This must result in a much lower average electrostatic potential than in DFT. The question is, if the results are compatible with electrochemical data. The answer is yes, and we shall demonstrate this in this article on two examples.

The inner potential is related to the potential of zero charge (pzc) of an electrode. We therefore complement our work with the investigation of the pzc of a few systems. For this purpose we use a scheme based on charge variation, which has been proposed in a recent work,[13] but so far has not been employed.

The rest of the article is organized as follows: After a brief literature review we investigate the inner and the surface potentials of water with DFTB, and then we present calculations of the pzc for Au(111) in contact with water, followed by consideration of pristine graphene and graphene with a vacancy. The technical details are presented in the appendix.

The Inner Potential of Water

Attempts to calculate the electrochemical inner potential by DFT

The relation between the physical and the electrochemical inner potentials has been investigated in a series of papers[12,14–17] that have received little attention in the electrochemical community. They all agree that the physical value is the spatially averaged electrostatic potential. Both experiment and high level DFT calculations give positive values of the order of 3.5–4.5 V with respect to the vacuum.

There have been several attempts to calculate the electrochemical value by DFT using various schemes. A recipe proposed by Kathmann et al.[15] consists in averaging the electrostatic potential only over regions of space with a low electronic density, which is meant to reproduce the region accessible to ions. By restricting the sampling to regions with an electronic density less than 0.01 e/bohr^3, they obtained reasonable agreement with electrochemical estimates of the inner potential. While this prescription nicely points at the heart of the problem, the limit is somewhat arbitrary.

Yu Shi and Beck[18] have calculated the free energy of hydration of a Na^+ ion in water, and obtained a value of about -3.9 eV for the bulk part. The experimental value for the real free energy of hydration, which includes the surface term, is about -4.4 eV, resulting in a surface potential of about -0.5 eV. Of course, this approach is not wholly theoretical since it relies on a comparison with experiment.

Solvated ions experience the electrostatic potential in the region they occupy. This cannot be calculated directly by DFT, but it can by estimated from the potential inside a suitable cavity. One approach consists in creating a spherical hole inside the ensemble and sampling the electrostatic potential inside,[19] in the other approach a noble gas atom is inserted into the water, and the potential is sampled at the position of the atom excluding the contribution from the atom itself.[20] Both approaches give small absolute values for the inner potential, of the order of ± 200 mV, consistent with the old estimate of Battisti and Trasatti.[5] The potential in the holes decrease with the radius, and depend somewhat on the basis set that is used. The values obtained with the noble gas atoms show no systematic trend, but are of the same order of magnitude. These results suggest that the inner potential experienced by an ion depends on its size, but that the dependence is weak.

In total, the role of DFT is somewhat contradictory: On the one hand, it gives good results for the conventional solvation energies of ions (without the surface term), and can, for example, be used to calculate the potential of mean force (pmf) of an ion as it approaches an electrode. But on the other hand, the inner potential obtained from DFT cannot be used to interpret the pmf, nor to explore the potential in the double layer. Calculations with holes or with noble gases are useful for understanding the meaning of the inner potential, but are not a viable method for exploring the inner potential in the double layer region.

As we shall show, DFTB offers the possibility to explore all aspects of the metal/electrolyte interface, including the distribution of the inner potential, within the same framework.

Results obtained by DFTB

The energetics of DFTB emulate normal DFT, but the electrostatic potential is calculated from the partial charges of the atoms, rather than from the localized nuclei and the delocalized electrons, and is thus similar to the method used in classical models. It is thus an interesting combination of the concepts of DFT and of the classical models. The distribution of the net charge of each atom is assumed to be a decaying exponential function. This results in a smoothly varying electrostatic potential without the $1/r$ singularities of the nuclei, which are screened by the electrons of the neutral atoms. In particular, positive and negative charges are treated at an equal level of localization.

Research Article
doi.org/10.1002/celc.202300230

In classical models of water the charges on the molecules are fixed. In contrast, in DFTB the charges depend on the interaction with the surroundings, and fluctuate. They are calculated self-consistently from the occupation of the atomic orbitals.

We have investigated the inner potential by DFTB following the setup by Leung.[14] The ensemble contained 128 water molecules in a box with dimensions 12.5 Å×12.5 Å×55 Å, – details are in the technical section at the end.

The result is shown in Figure 1. Due to the finite size of the ensemble, the particle profiles for hydrogen and oxygen still show minor oscillations in the bulk with a wavelength of about 3 Å, corresponding to the size of a water molecule. At both ends the profiles decay over a distance of about 4 Å, the hydrogen profiles extending a little further into the vacuum region.

Together with the particles we sampled the electrostatic potential on a mesh of 12×12×55 points, over which we averaged and symmetrized – see Figure 2. The absolute value of the potential has no meaning, the important point is the difference between the potential inside and outside. Outside the water film the potential is constant with a value of 0.16 V,

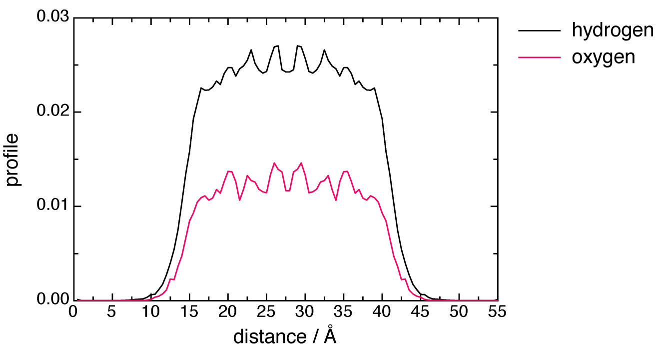

Figure 1. Density profiles of the hydrogen and oxygen atoms in the *z* direction, which is the longer extension of the simulation box, and where the system is bounded by vacuum. The units on the vertical axis are arbitrary.

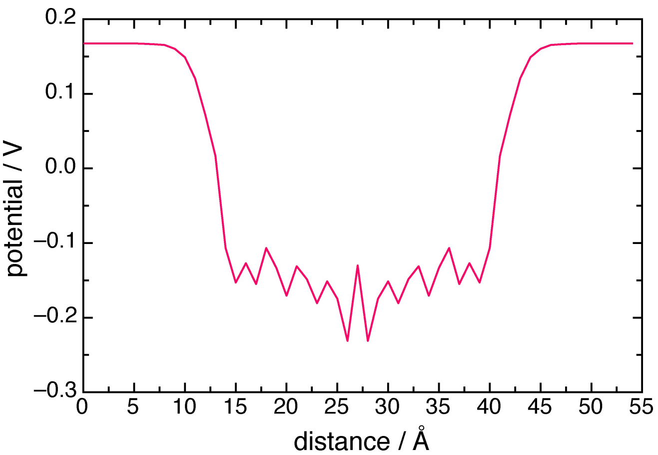

Figure 2. Average electrostatic potential along the *z* direction, which is the longer extension of the simulation box and where the system is bounded by vacuum.

inside the potential fluctuates around an average value of −0.16 V, resulting in an estimate of −0.32 V for the surface potential of water. The absolute value is somewhat smaller than that predicted by most classical models of water, or from the solvation energy of Na^+ obtained from DFT, a little higher than the estimate of Trasatti and Baitisti, and close to the estimates based on DFT calculations for holes or noble gas atoms.

We repeated the calculations with a slightly different parameter set for water, which gives slightly better radial distribution functions for water.[21] The result for the inner potential, −0.24 V, is the same within the numerical error.

In addition, we performed standard DFT simulations, using a smaller ensemble of 23 water molecules, and obtained values of about 3.32 V, which are of the order of the published DFT values. This was the point we wanted to prove.

Work Function and Potential of Zero Charge

Au(111) from DFTB

The work function is the energy needed to remove an electron from the electrode, and can therefore be calculated from the change of the free energy with the charge. This opens an alternative path for obtaining the work function by calculating the free energy for small excess charges. In DFT and in DFTB an excess charge is always compensated by a uniform background charge, so that the results have to be corrected.[22] Kajita et al.[23] have performed corresponding DFT calculations for a Au(111) surface in the vacuum and shown, that this method gives the correct work function, provided the system is large enough to avoid finite size effects.

The correction for the presence of the background charge consists of two terms.[22,23] A self energy term of the background, and the interaction of the background with the average electrostatic potential. Making the corrections is cumbersome, so an attractive strategy is to use only small excess charges where the correction is negligible. Since the correction scales with the square of charge the work function can be obtained from the slope for vanishing excess charge.

Figure 3 shows the energy of our Au(111) slab without water as a function of the excess charge on the system. Over the investigated range of charge the plot is almost linear. From the slope at zero charge we obtain a work function of 5.15 eV, which compares quite well with the experimental value of 5.33 eV.[24] In a similar way, we have calculated the work functions of Ag(100) and Li(100) from DFTB and obtained values of $\Phi = 4.07\,(4.21)$ eV for Ag(100) and $\Phi = 3.04\,(2.96)$ eV for Li(100), where the experimental values are given in parentheses.

The potential of zero charge on the vacuum scale is given by the work function of an electrode surface covered with a layer of solution, which in turn is in contact with the vapor or the vacuum. This free surface may create practical difficulties, so we first look at a simpler system. It is easier to fill the space between two electrodes completely with water, but then the surface potential of water is not contained in the system, and has to be added a posteriori.

Chemistry Europe
European Chemical Societies Publishing

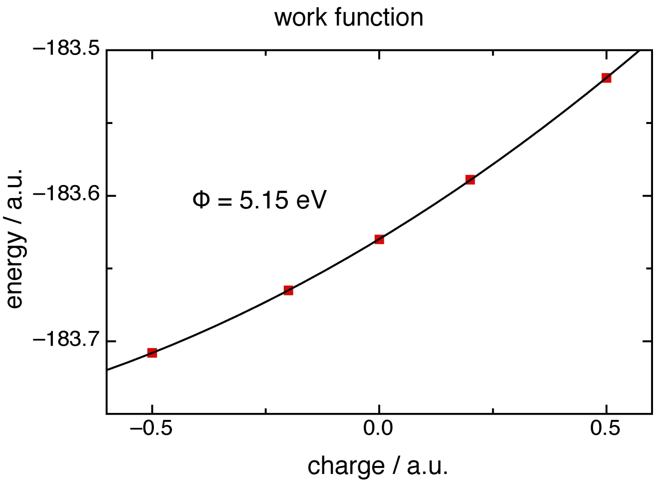

Figure 3. Free energy of a Au(111) electrode in vacuo as a function of the charge on the electrode; the zero of the energy scale is arbitrary. 1 a.u. of charge corresponds to 5.75 μCcm^{-2}.

For gold immersed in water the plot is linear over a wider range – see Figure 4. Water screens the potential generated by the background charge well and reduces the correction term. The slope gives a value of 5.44 V for the pzc on the vacuum scale. As pointed out above, the surface potential of water must be added to this, resulting in a total value of $\phi_{pzc} = 5.76$ V; the experimental value, based on a value of 4.44 V for SHE on the vacuum scale, is 4.94 eV.

The error in the absolute value is less important than the fact that the calculated work function in the presence of water is higher than in the absence, while experimentally it is lower by about 0.5 eV. An examination of the charge distribution at the gold/water interface shows that at the pzc there is a slight negative excess charge of about -5×10^{-2} a.u. on each surface atom of gold, which is compensated by a corresponding positive charge in water. This has also been observed by DFT-based simulations.[16] While this effect would lower the work function, in our results it is more than compensated by a net orientation of the water adjoining the surface, with the hydrogen end pointing slightly towards the surface.

We surmise that the main reason for the discrepancy lies in the deficiencies of DFTB to fully describe all aspects of the water-water interaction, especially the electrostatic interactions beyond the monopole-monopole term. Of course, this could be corrected (and there is ongoing work to include multipoles in DFTB), but the present work is meant to be an exploration of the method, a proof of concept rather than a quantitative work.

We have also performed calculations for a Au(111) electrode covered by a layer of water 20 Å thick with 25 Å of vacuum on top. Such a large vacuum layer avoids problems with the cyclic boundary conditions, where water molecules can escape and wander to the back side of the electrode. In DFTB the vacuum layer costs almost nothing in terms of computation time. The water layer proved to be stable. A plot of the free energy vs. the charge resulted in a pzc of 5.43 eV on the absolute scale (see Figure 5), which compares well with the value of 5.76 eV obtained above, and is somewhat closer to the experimental value. Thus a direct simulation of the pzc as the work function is also a feasible path. From a numerical point of view it is somewhat easier to determine the surface potential of water once and for all, and for a specific metal set up two electrodes and fill the space between with water. In this case both systems are symmetric, which helps in the evaluation of the results.

Graphene from DFTB

Graphene is well described by DFTB; indeed, our basic understanding of the unusual properties of graphene is based on a simple tight binding model, so a sophisticated version like DFTB should do well. We have therefore investigated two different kinds of graphene immersed in an aqueous solution: pristine graphene, and graphene with a single vacancy. Figure 6 shows the energy for both systems in vacuum as a function of the charge. The plots are linear over the total range investigated; but note that the electrode area with 507 Å^2 is quite large. From the slope we obtain a work function of 4.52 eV for pristine

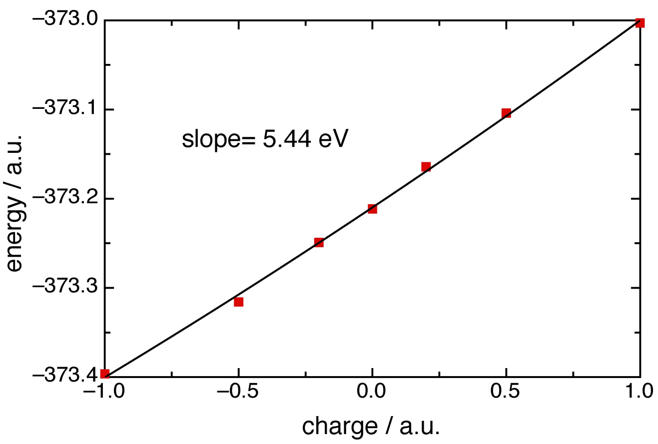

Figure 4. Free energy of a Au(111) electrode immersed in water as a function of the charge on the electrode; the zero of the energy scale is arbitrary.

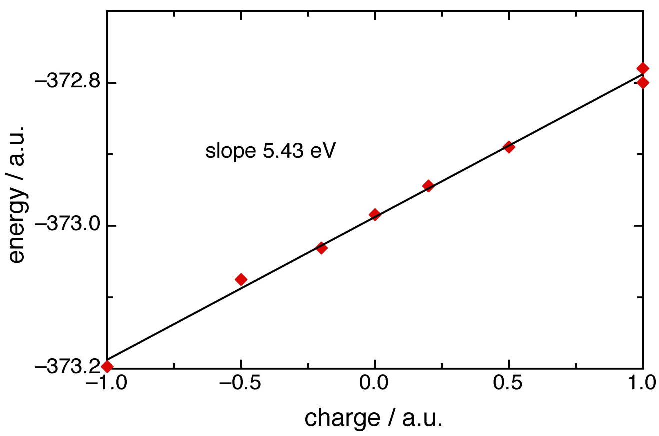

Figure 5. Free energy of a Au(111) electrode covered by a 20 Å film of water as a function of the charge on the electrode; the zero of the energy scale is arbitrary.

Research Article
doi.org/10.1002/celc.202300230

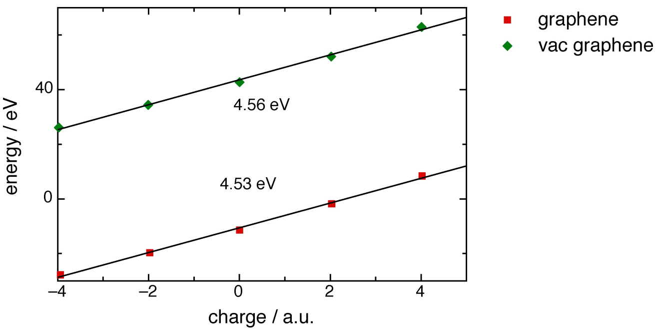

Figure 6. Energy of pristine graphene and graphene with a vacancy as a function or the charge on the electrode; the zero of the energy scale is arbitrary. One unit charge corresponds to a surface charge density of 1.58 μCcm^{-2}.

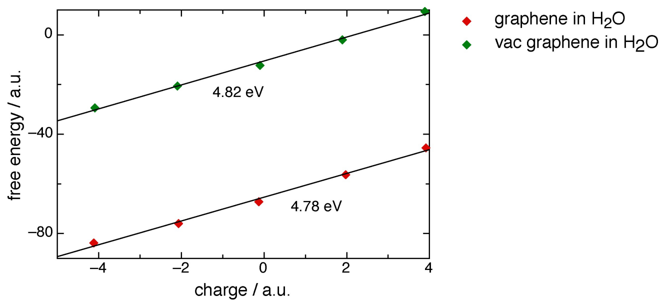

Figure 7. Free energy of pristine graphene and graphene with a vacancy immersed in water as a function or the charge on the electrode; the zero of the energy scale is arbitrary.

graphene, which compares well with the experimental value of about 4.6 eV.[25] The vacancy leaves the work function practically unaffected.

Figure 7 shows the corresponding plot for graphene immersed in water. The experimental value for the pzc of pristine graphene is 0.243 V vs. SHE.[26] Using a value of 4.44 V for SHE on the absolute scale, this results in a value of 4.68 V for the pzc. The slope of the free energy vs. charge plot for the immersed electrode gives a value of 4.72 V, which is in excellent agreement. However, as pointed out above, we have to add the surface potential of water, which is 0.32 V, which makes the agreement still tolerable. In particular, we obtain a pzc which is a little higher than the work function. In our calculations the pzc for graphene with a vacancy also differs only little from the values for pristine graphene. Since our graphene electrode is quite large and contains only a single vacancy, this is understandable. Thus for graphene with a vacancy in contact with water we obtain a value of $(4.72+0.32)$ eV$=$5.05 eV. Experimental values for graphene with vacancies depend on the preparation of the sample, so they cannot be compared with our calculations.

A note on arbitrary electrode potentials

The relation:1

$$\left(\frac{\partial G}{\partial N_e}\right)_{p,T} = \tilde{\mu}_e = \mu_e - e_0\phi \tag{1}$$

where G is the free energy of the system, and the suffix e denotes electrons, holds for a charged electrode as well. However, the total system must be electrically neutral, so that the charge on the electrode must be compensated. This implies a model for a double layer. If nothing is specified, both DFT and DFTB automatically add a compensating background charge. The system then corresponds to the double layer model of Neurock et al.[27] Any excess charge is localized on the surface of the electrode, and, except for extremely high charges, should leave the chemical potential μ_e unchanged. Eq. (1) can then be used to determine the electrode potential. The same procedure can be used if the double layer is represented by an implicit electrolyte. Indeed, theoretically an explicit electrolyte could also be used, but then the simulation become computationally very expensive.

Conclusions

Using molecular dynamics based on DFTB, we have investigated the inner potential of water, and the work functions and pzcs of Au(111) and graphite. For the inner potential we obtained a value of about -0.32 eV, which is in the range of the values believed to be relevant for electrochemistry, and much lower than the physical values of 3.5 to 4.5 eV observed by electron scattering or by high level DFT.

We calculated the work function and the pzcs by varying the charge on the electrode. This method is convenient for the pzc, since it requires the free energies of the systems only, and not the average distribution of the electrode potential. In addition, in the presence of water the correction for the excess charge can be ignored, since the potential is well screened by the dipole moments.

For Au(111) we obtained a good value for the work function, while the pzc came out a little high. This could probably be improved by re-calibrating the Slater–Koster files for the interaction of water with gold. For graphite, both the work function and the pzc came out well, since the required parameter files have been optimized for decades. Also, when comparing experiment with theory, one has to bear in mind experimental errors caused, e.g. by anion adsorption, and the uncertainty in the value of SHE on the vacuum scale.

All in all, DFTB gives a good description of the electrochemical interface with a potential distribution that is relevant for electrochemical reactions, and more useful than results from DFT. This fact, combined with the speed of the code, makes DFTB an attractive method for computational electrochemistry. The only caveat is the scarcity of reliable Slater–Koster parameter files for metal / water interfaces.

1 This paragraph was instigated by the question of a referee.

Computational Method

DFTB calculations

All calculations were performed with a density functional tight binding model using the DFTB+ software package.[28] In DFTB, the interactions are parametrized in the so called Slater–Koster files, which makes molecular dynamics simulations considerably faster than with DFT. We have used the 3ob-3-1 set,[29,30] which has been shown to give good results for water. As mentioned in the text, additional calculations have been performed using the modified set proposed by Goyal et al.[21] Calculations of solid gold as well as gold-water interfaces employ the auorg-1-1 set,[31] whereas the Au–H and the Au–O repulsive potentials have been re-parameterized. The modified parametrization files are provided in the supplementary materials. The new repulsive potentials have been fitted using the constrained splines (CCS)[32,33] methodology, with adsorption energies calculated by ab initio PBE calculations as references. We resorted to the switch constraint and to the strictly repulsive constraint for the Au–H and the Au–O interaction, respectively. The reference data was generated using the Au(111) surface, with a hydrogen and an oxygen atom being placed at different distances and positions over the surface.

The DFTB parameters for gold give good results only when the lattice is kept fixed. So in the MD for gold and water only the latter molecules were allowed to move. In contrast, in the graphene-water systems all atoms were free to move without constraints. For this system, dispersion corrections were applied within the DFT-D3 option based on the Grimme scheme.[34] For the gold-water system we performed calculations both with and without dispersion. They made no difference to the results except an overall shift of the energy.

For gold/water, the Brillouin-zone integration was performed using a 4×4×4 k-point Monkhorst-Pack grid.[35] Simulations using Gamma point integration gave essentially the same results.

For the inner potential of water, following Leung, we set up an ensemble of 128 water molecules in a box with original dimensions 12.5 Å×12.5 Å×25 Å. We let this system relax to equilibrium; subsequently the system was extended to 55 Å in the z direction, so that it could relax in this direction. The system was allowed to relax to equilibrium in a series of MD runs in the NTV ensemble of 5000 time steps at first 0.1 fs, later 0.3 fs using a Berendsen thermostat with a time constant of 0.3 fs, later 3 fs. After ten such runs the average free energy was constant, and the system was taken to be in equilibrium. More precisely, the system is in a metastable state, since finally the water would vapourize.

The Au/water system consisted of a box of 12.67 Å×10.97 Å×22 Å with two layers of gold and 69 water molecules, resulting in a density of 1 $g\,cm^{-3}$ for water.

For the Au in vacuum the extension in the z-direction was varied between 22 Å and 100 Å without affecting the results.

Supplementary simulation have been performed with VASP using the PBE functional, Gamma point integration, a Lagrange thermostat, and Grimme corrections[34] for the dispersion interactions. Additional calculations for the work function of Li have been performed with the parametrization of Li and Qi,[36] and for Ag the parameter set hyb-0-2[37] was used.

Acknowledgements

The authors acknowledge support by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through Grant No. INST 40/575-1 FUGG (JUSTUS 2 cluster). We thank Prof. Stephan Irle from Oakridge National Laboratory for providing us with his Slater–Koster files for water. T. v. d. Heide acknowledges financial support from the German Research Foundation (DFG) through Grant No. FR2833/76-1.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: DFT · inner potential · potential of zero charge · tight binding · work function

[1] M. Elstner, G. Seifert, *Philos. Trans. R. Soc. London Ser. A* **2014**, *372*, 20120483.
[2] S. Fletcher, *J. Solid State Electrochem.* **2020**, *24*, 3029.
[3] W. Schmickler, E. Santos, *Interfacial Electrochemistry* 2nd edition, Springer Verlag, Berlin, 2010.
[4] E. Santos, W. Schmickler, *J. Solid State Electrochem.* **2023**, https://doi.org/10.1007/s10008-023-05521-x.
[5] A. De Battisti, S. Trasatti, *Croat. Chem. Acta* **1976**, *48*, 607.
[6] H. Bethe, *Ann. Phys. (Leipzig)* **1928**, *87*, 55.
[7] A. Harscher, H. Lichte, *Proc. ICEM14* **1998**, *1*, 553.
[8] T. Prozorov, T. P. Almeida, A. Kovács, R. E. Dunin-Borkowski, *J. R. Soc. Interface* **2017**, *14*, 0464.
[9] N. N. Yesibolati, S. Lagana Hongyu Sun, M. Beleggia, M. Kathmann, S. M. Kasama, T. K. Molhave, *Phys. Rev. Lett.* **2020**, *124*, 065502.
[10] S. Sakong, A. Groß, *J. Chem. Phys.* **2018**, *149*, 084705.
[11] P. Li, J. Huang, Y. Hu, S. Chen, *J. Phys. Chem. C* **2021**, *125*, 3972–3979.
[12] S. M. Kathmann, L. F. Kuo, C. J. Mundy, *J. Am. Chem. Soc.* **2008**, *130*, 16556.
[13] E. Santos, W. Schmickler, *Curr. Opin. Electrochem.* **2023**, *28*, 101208.
[14] K. Leung, *J. Phys. Chem. Lett.* **2010**, *1*, 496–499.
[15] S. M. Kathmann, I.-F. W. Kuo, C. J. Mundy, G. K. Schenter, *J. Phys. Chem. B* **2011**, *115*, 4369–4677.
[16] L. Jiabo, M. Iannuzzi, A. Cuesta, J. Cheng, *Phys. Rev. Lett.* **2017**, *119*, 016801.
[17] B. Sellner, S. M. Kathmann, *J. Chem. Phys.* **2014**, *141*, 18C534.
[18] Y. Shi, T. L. Beck, *PNAS* **2020**, *117* (48), 30151.
[19] R. C. Remsing, M. D. Baer, G. K. Schenter, C. J. Mundy, J. D. Weeks, *J. Phys. Chem. Lett.* **2014**, *5*, 2767.
[20] M. R. Becker, P. Loche, R. R. Netz, *J. Chem. Phys.* **2022**, *157*, 240902.
[21] P. Goyal, H.-J. Qian, S. Irle, X. Lu, D. Roston, T. Mori, M. Elstner, Q. Cui, *J. Phys. Chem. B* **2014**, *118*, 11007.
[22] A. Y. Lozovoi, A. Alavi, J. Kohanoff, R. M. Lynden Bell, *J. Chem. Phys.* **2001**, *115*, 1661.
[23] S. Kajita, S. T. Nakayama, J. Yamauchi, *J. Phys. Conf. Ser.* **2006**, *29*, 120.
[24] G. N. Derrya, M. E. Kern, E. H. Worth, *J. Vac. Sci. Technol. A* **2015**, *33*, 06080.
[25] O. Leenaerts, B. Partoens, F. M. Peeters, A. Volodin, C. Van Haesendonck, *J. Phys. Condens. Matter* **2017**, *29*, 035003.
[26] J. Poon, C. Batchelor-McAuley, K. Tschulik, R. G. Compton, *Chem. Sci.* **2015**, *6*, 2869–2876.

[27] C. D. Taylor, S. A. Wasileski, J. S. Filhol, M. Neurock, *Phys. Rev. B* **2006**, *73*, 165402.
[28] B. Hourahine, B. Aradi, V. Blum, F. Bonafe, A. Buccheri, C. Camacho, C. Cevallos, M. Y. Deshaye, T. Dumitrica, A. Dominguez, S. Ehlert, M. Elstner, T. van der Heide, J. Hermann, S. Irle, J. J. Kranz, C. Köhler, T. Kowalczyk, T. Kuba, I. S. Lee, V. Lutsker, R. J. Maurer, S. K. Min, I. Mitchell, C. Negre, T. A. Niehaus, A. M. N. Niklasson, A. J. Page, A. Pecchia, G. Penazzi, M. P. Persson, J. Jezác, C. G. Sanchez, M. Sternberg, M. Stöhr, F. Stuckenberg, A. Tkatchenko, V. W. Yu, T. Frauenheim, *J. Chem. Phys.* **2020**, *52*, 124101.
[29] M. Gaus, A. Goez, M. Elstner, *J. Chem. Theory Comput.* **2012**, *9*, 338.
[30] https://dftb.org/
[31] A. Fihey, C. Hettich, J. Touzeau, F. Maurel, A. Perrier, C. Köhler, B. Aradi, T. Frauenheim, *J. Comb. Chem.* **2015**, *36*, 2075.
[32] K. A. Kandy, E. Wadbro, B. Aradi, P. Broqvist, J. Kullgren, *J. Chem. Theory Comput.* **2021**, *17*, 1771.
[33] A. Krishna, E. Wadbro, C. Köhler, P. Mitev, P. Broqvist, J. Kullgren, *Comp. Phys. Commun.* **2021**, *258*, 107602.
[34] J. Grimme, S. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
[35] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188.
[36] Y. Li, Y. Qi, *J. Phys. Chem. C* **2018**, *122*, 10755.
[37] B. Szuecs, Z. Hajnal, R. Scholz, S. Sanna, T. Frauenheim, *Appl. Surf. Sci.* **2004**, *234*, 173–177.

Manuscript received: May 22, 2023
Revised manuscript received: July 27, 2023
Version of record online: September 26, 2023