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Ab initio molecular dynamics simulation of liquids and solutions

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Abstract. This contribution is a short overview of some of the highlights in the application of density functional based *ab initio* molecular dynamics methods to aqueous liquids and their chemistry. Recent progress in the study of liquid water at neutral and finite pH is discussed in some detail, such as the first principles computation of the molecular dipole moment in the liquid and the equilibrium constant for auto-dissociation. Also mentioned are some recent simulations of chemical reactions in aqueous solutions. We conclude with an outlook for the near future.

Modelling and computer simulation have played a vital role in our understanding of liquids. The use of numerical methods has enabled us to characterize and quantify the finite temperature fluctuations which stabilize the liquid phase and distinguish it from the solid state. Dynamical disorder is also the decisive factor that makes liquids a suitable medium for chemical reactions. Diffusive and reorientational motion gives solvent molecules the freedom to make way for solvated reactive species, allowing them to assume the often highly specific configurations required for a successful reactive encounter. Polar solvents have the further crucial function of assisting in the separation of charged products. An all important example of a polar solvent is, of course, water. What is unique for this most famous among solvents is the ability of water molecules to form strong hydrogen bonds to ionic or polar solutes and at the same time maintain hydrogen bonding to fellow water molecules in the surrounding solvent. Multiple hydrogen bonding is the explanation for why water is capable of stabilizing ionic species that hardly exist anywhere else. However, the tendency of water to directly participate in a reaction, either as reactant or catalyst, makes aqueous reactions complex and difficult to control. This is the reason that water, in fact, is one of the less popular solvents in organic chemistry laboratories. Living organisms, on the other hand, have learned to exploit these properties and water is the preferred solvent in biochemistry. Water also plays a crucial role in electrochemistry.

Computer modelling has already made essential contributions to unravelling the complexity of aqueous solutions. In particular it has helped us in rationalizing the activity of biomolecules. Numerical simulation is certain to play a similar role in the study of reactive solutions, such as water at non-neutral pH. However, owing to the lack of reliable force fields, aqueous chemistry has eluded treatment by atomistic modelling so far. This situation is rapidly changing now as a result of advances in *ab initio* molecular dynamics (MD) methods [1]. This still relatively new technique in computational chemistry combines the powerful density functional theory (DFT) approach [2] to electronic structure calculation with simulation of finite temperature dynamics, thus avoiding parametrized force fields altogether.

A first priority in the application to liquids was verifying that the accuracy of DFT is sufficient to describe the comparatively weak intermolecular interactions. For aprotic solvents, dominated by Van der Waals forces, the technical difficulties have not been fully resolved yet

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(see e.g. [3]). Also for water, a number of the currently available density functionals fail the test, producing disordered structures with unrealistically slow diffusion and reorientation times. The functional developed by Becke, Lee Yang and Parr, however, was found to be able to stabilize liquid conditions at ambient temperature yielding structural and dynamical properties in excellent agreement with experiment [4]. Using this approach Silvestrelli *et al* determined the effective molecular dipole moment in liquid water [5]. The value they obtained is 3.1 D, almost the double of the 1.85 D in vacuum. This result is a good illustration of how *ab initio* MD can be used to obtain data that cannot be directly deduced from experiment. Also from a more technical point of view this computation represents a major step forward. It required overcoming the difficulty of identifying molecular entities in the collective extended DFT electronic ground state which makes no such distinctions. Thus, by using a localization scheme [5] Silvestrelli and coworkers succeeded in recovering the molecular description of the liquid.

The encouraging results for pure water gave the green light for a series of *ab initio* MD applications to simple acidic and basic solutions. A milestone here was the detailed examination of the excess proton in water by Tuckerman *et al* [6] which contributed to resolving the old controversy about the role of the $H_5O_2^+$ (Zundel) and $H_9O_4^+$ (Eigen) cation. When these ions are viewed embedded in the hydrogen bonded network of the surrounding liquid, they turn out to be two phases of the same fluctuating complex. The simulation showed that the dynamical rearrangements in the pattern of hydrogen bonds driving the interconversion of these two structures are also the key to the explanation of the structural (Grotthuss) diffusion of the solvated proton (see also [7]). Subsequent investigations of two prototypical strong aqueous acids, sulphuric and hydrochloric acid, are extensions of the excess proton work and confirmed that DFT estimates for the pH of these solutions are in the correct range of values. Recent path integral *ab initio* MD calculations by Marx *et al* [7], addressing the role of proton quantum effects, have validated and refined this picture.

Weak acids pose more of a technical problem, because of the highly activated nature of proton release. A first attempt to determine the equilibrium constant for the auto-dissociation of water by Trout and Parrinello [8] resulted in a value of $pK_w = 13$, corresponding to a (free) energy of ≈ 18 kcal mol^{-1} (the experimental pK_w value is 14). It is, of course, completely out of the question that an endothermic process requiring this much energy can be observed as a spontaneous event in an MD simulation. The approach often used to overcome this difficulty is forcing the system to undergo the reaction by controlling a relevant reaction coordinate. In MD this can be conveniently achieved by mechanical constraint methods. This approach would be of very limited use if it did not also enable us to compute the corresponding relative free energies. Constraint methods satisfy this requirement because the (weighted) average of the force of constraint can be identified with the mean force [9]. Therefore, relative free energies can be directly obtained by numerical integration of the average forces of constraint.

Applying this approach, Trout and Parrinello performed their calculation of pK_w by pulling off a proton from a selected water molecule, thus inducing a dissociation reaction. They fixed the length of one of the OH bonds at increasingly larger distances using a simple distance constraint. It was found that for OH distances beyond 1.3–1.4 Å the bond is effectively broken and the constrained proton was seen to associate with neighbouring water molecules forming a OH_3^+ ion, leaving behind a hydroxyl, OH^-, counterion. Most of the activation energy of 18 kcal mol^{-1} is spent on the formation of this OH^-–OH_3^+ contact-ion pair. The free energy cost for further charge separation is minimal. However, there is no constraint on the two protons in the hydronium which were already there as part of the original H_2O molecule and these protons are free to leave. This was, in fact, observed to occur spontaneously even on the picosecond time scale of the *ab initio* MD simulation [8]. Once these protons wander off in the solution, there is nothing to stop them recombining with the hydroxyl and this was eventually the fate of all of them. This sudden reversal of the reaction is the consequence of ignoring the identity of protons in the bond constraint that was applied. Each proton can substitute for another in chemical functions. This instability was resolved in [10] by using, instead of a constraint for a specific OH bond, a constraint on the coordination of an oxygen atom. This coordination constraint scheme does not distinguish between protons. It can be used to stabilize any short lived conjugate base of weak acids in studies of acid or base catalysed reactions.

Ab initio MD is ready to be employed in investigations of reaction mechanisms in solution. Examples of studies that have been recently completed, or are currently under way, concern acid catalysed addition of water to a carbonyl group [11], ligand substitution of an aqueous *cis*-platin complex [12] and the reaction of dinitrogen and hydroxyl radicals in water [13]. In all of these cases the *ab initio* MD clearly exposed the concerted nature of the processes in aqueous chemistry. Looking ahead, an important task for the near future will be the quantitative characterization of reactivity in water and other protic solvents. In particular the first principles computation of pK, redox potentials, activation energies and, ultimately, reaction rates is a major challenge. Another topic which is already the subject of intensive ongoing research is the development of methods for the evaluation of the response functions determining optical and NMR spectra of liquids. A first example is the computation of the infra-red absorption spectrum of water by Silvestrelli *et al* [14]. *Ab initio* molecular dynamics may very well be the only way to deal with this level of complexity in which electronic states are strongly coupled to the thermal disorder in liquids.

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