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# ***Ab initio* molecular dynamics simulation of liquids and solutions**

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**Abstract.** The application of *ab initio* molecular dynamics simulation to bulk molecular systems is reviewed with emphasis on the density functional treatment of intermolecular interactions. Examples discussed are water, hydrogen fluoride, benzene, and sulphuric acid.

## **1. *Ab initio* molecular dynamics**

Advances in the density functional theory (DFT) method of electronic structure calculation justify an optimistic outlook for the application of *ab initio* molecular dynamics (MD) to solution chemistry. The *ab initio* MD method [1] combines a DFT description of the electronic structure of molecules with finite-temperature dynamics of atoms. The forces on atoms are derived at each time step directly from the instantaneous (adiabatic) electronic states, thus avoiding the necessity of parametrized interatomic interaction models (for a review of the *ab initio* MD method, see e.g. reference [2]; for a textbook on the use of DFT methods in chemistry, see reference [3]). Part of the motivation for using the DFT approach is its computational efficiency in treating large (periodic) systems. This enables us to include bulk solvent in the *ab initio* calculation and study the dynamics of the reaction and the coupling to the solvent at the same level of approximation. The simulation of molecular liquids, however, is particularly demanding for electronic structure calculation methods because inaccuracies of only  $10^{-3}$  au ( $\approx 300$  K) in the intermolecular interaction energies, which are very small on the atomic energy scale, are sufficient to perturb the structure and dynamics of the liquid. After introducing the relevant DFT technology, I shall summarize the experience gathered by recent *ab initio* MD studies of bulk molecular systems.

## **2. Density functionals**

The basic reason for the popularity of DFT is the fact that the relatively simple local density approximation (LDA) to the energy functional is for many properties a good first approximation [4, 5]. Unfortunately, the accuracy of energies in LDA, both intra- and intermolecular, is still insufficient for a realistic simulation of chemical reactions in liquids. The DFT description of the energetics of bond formation was improved considerably by extending the local energy functional with terms that depend also on the gradient of the electron density. This so-called generalized gradient approximation (GGA) has been an

enormous stimulus to research on DFT. The literature on the performance of gradient corrections (GCs) is rapidly growing [4, 5, 6, 7], whereas the analysis at a more fundamental level is also progressing (see e.g. references [8, 9]). It has been recognized now that a crucial step for applications in chemistry was taken by Becke, who constructed a relatively simple GC for exchange effects [10]. The GGA with this exchange-only GC is usually referred to as B. It can be combined with further GCs for correlation energy, of which the functionals developed by Perdew (P) [11] and Lee, Yang and Parr (LYP) [12] are the most widely used. These GGA functionals for exchange and correlation are known by the acronyms BP and BLYP.

### 3. Hydrogen-bonded liquids: water and HF

The Becke GC proved to be crucial for the DFT description of hydrogen bonding. In the LDA the water dimer is overbound by as much as  $15 \text{ kJ mol}^{-1}$  [13, 14] (compared to an experimental binding energy of  $\approx 22 \text{ kJ mol}^{-1}$ ), with an O–O equilibrium distance,  $R_{OO}$ , which is almost  $0.3 \text{ \AA}$  too small. The B exchange correction expands  $R_{OO}$  to approximately the correct value, however, underestimating the binding energy by  $10 \text{ kJ mol}^{-1}$  [14]. When a GC for correlation is included, a binding energy of  $18 \text{ kJ mol}^{-1}$  is obtained [14] (see also reference [7]). A dramatic illustration of the reduction of the effective repulsive radius of water molecules in LDA is the effect on the high-pressure equation of state of ice. At experimental densities in the 100 GPa regime LDA yields vanishing or even negative pressures [15]. B [16] and BP [15], on the other hand, yield values for the pressure that are in good agreement with experiment.

The next critical test of the new generation of GC density functionals was the application in the *ab initio* simulation of liquid water [17]. The encouraging outcome was that the MD system (32 molecules in a cubic periodic cell) was indeed in the liquid state with, to a very good approximation, the correct structure and dynamics [14, 17]. Moreover, comparison of the various GGA functionals (B, BP and BLYP) showed that, whereas correlation effects are secondary for hydrogen bonding, they cannot be ignored at the level of the subtle balance of forces and thermal motion in the liquid. The effective strength of the hydrogen bonding in the liquid was found to be stronger in BP and weaker in B relative to BLYP. This is reflected in an overstructuring of the radial distributions for BP and an understructuring for B with respect to the  $g$  of  $r$ 's for BLYP, which also yielded excellent agreement with experiment [14]. Whereas these differences in structure are minor, the effect on the relaxation dynamics was found to be more substantial. For example, the self-diffusion in BP water is slowed down to  $D = 0.035 \text{ \AA}^2 \text{ ps}^{-1}$ . Consistent with the results for the  $g$  of  $r$ 's, diffusion in BLYP and B water is faster ( $D = 0.13$  and  $D = 0.23 \text{ \AA}^2 \text{ ps}^{-1}$ , respectively) [14]. Considering the fact that (for technical convenience) the MD sample is deuterated, the dynamics of BLYP appears to be the closest to the experimental value of  $D = 0.24 \text{ \AA}^2 \text{ ps}^{-1}$  in light water.

Another hydrogen-bonded liquid that has been investigated by *ab initio* MD simulation is hydrogen fluoride [18]. DFT calculations for the HF dimer show a trend similar to that for water when various GGA are compared [18], i.e. LDA is seriously overbound, B underbound, and BP and BLYP in reasonable agreement with experiment. Orientational relaxation and diffusion in a periodic system consisting of 54 molecules at 290 K (using BLYP) were found to proceed at a time-scale comparable to that for experiment, confirming that the system was liquid. The structural properties turned out to be more interesting compared to those of water for which adequate potential models (empirical or *ab initio*) can 'in principle' be constructed. One of the results obtained by the *ab initio* simulation in reference [18] was a significant shortening of the nearest-neighbour FF distance (from

$R_{\text{FF}} = 2.8 \text{ \AA}$  in the dimer to  $R_{\text{FF}} = 2.5 \text{ \AA}$  in the liquid). This was interpreted as a collective effect in the hydrogen bonding, which gives the local structure in the liquid an almost quantitative resemblance to that of the solid. Indeed, a strong tendency to form (short-lived) zigzag chains, which are the characteristic structural motifs of the solid, was also observed in the liquid. In contrast, potential models fail to reproduce the  $R_{\text{FF}}$ -contraction. The corresponding radial distributions at short range are more reminiscent of the gas-phase dimer structure. The degree and type of association in liquid is rather different from the *ab initio* results, which are in much better agreement with the available experimental data.

#### 4. Aprotic systems: rare gas and benzene

For hydrocarbons, unlike for hydrogen-bonded systems, dispersion energy is crucial and the electrostatic contribution to the interaction energy is minor. A local or even semilocal density functional is in principle not capable of describing the attraction due to dispersion, because this interaction is a long-range nonlocal correlation effect. Hence, one would expect to find little or no binding for Van der Waals-type dimers, neither in LDA nor GC density functionals. However, in the minimum-energy configuration the charge clouds overlap and it turns out that the purely local exchange and correlation energy in the LDA functional provides an (erroneous) attraction. Noble-gas dimers are even overbound in LDA, as has been established by two recent, independent, high-accuracy calculations [19, 20]. The GGA changes the interaction of noble-gas dimers drastically as was also shown in references [19] and [20]. The noble-gas pair potentials for the B exchange-only functional is purely repulsive with no minimum. Including the P GC for correlation [20] or LYP [19] essentially gives the same result. Hence, at a qualitative level, the effect of introducing the B exchange GC is consistent for Van der Waals and hydrogen-bonded systems, namely an (over)compensation of the overbinding in LDA, leading, unfortunately, to vanishing binding of Van der Waals systems.

In view of the importance of hydrocarbons as aprotic solvents it would be interesting to quantify the effect of neglecting dispersion by (current) DFT methods in bulk systems. The results of such an evaluation can also be useful to assess the possibility of modelling the missing dispersion by a potential function, which is simply added to the DFT Hamiltonian. *Ab initio* MD simulation of Van der Waals liquids are (to the best of my knowledge) not available in the literature. Studies of solids, however, are equally, if not better, suited to exposing perturbations in the equation of state. Recently, a study of the low-pressure–low-temperature phase of solid benzene was completed [21], which verified that this molecular system follows the pattern of the noble gas. In LDA, the binding of the benzene dimer is, fortuitously, of the correct order of magnitude. For the B and BLYP dimer, however, the purely repulsive interaction dominates and is even able to cancel the electrostatic (quadrupole) coupling in the configurations where it is attractive.

The results for the solid are consistent with dimer interactions. LDA performs seemingly the best with a 15% higher density at zero pressure compared to experiment, whereas the B and BLYP solids are mechanically unstable, lacking any cohesion. Another measure of how the GGA affects the thermodynamic state is the pressure at the experimental zero-pressure-state point. For the B and BLYP solids this number has increased to 40 and 20 kbar, respectively, which would imply an unacceptable shift of the melting line. If, however, an  $r^{-6}$ -potential of an empirical model is used to represent the dispersion, the LDA solid shrinks to a zero-pressure equilibrium density that is 50% too large, whereas B and BLYP solids are stabilized at densities that agree with experiment within 10%. These results give us some confidence that, accepting an extension by an optimized empirical potential as a

practical remedy for the limitations of GGA DFT, the simulation of Van der Waals liquids is feasible for the purpose of accounting for the solvation of *ab initio* reactants in an aqueous environment.

## 5. Acidic solutions: the $\text{H}_3\text{O}^+$ ion and sulphuric acid

Acidic aqueous solutions are important examples of chemically active solvents because of their ability to catalyse chemical reactions by donating protons to or extracting them from solutes. Proton transfers, moreover, are processes on the picosecond time-scale and, hence, observable as spontaneous events in the *ab initio* MD time window. This makes acidic solutions ideal test systems. In reference [22] the structure and transport of a single proton solvated in a periodic sample of 32 water molecules was studied. In the vast literature on this fundamental system in aqueous chemistry the cationic complex that binds the excess proton is pictured, either as a hydronium ( $\text{H}_3\text{O}^+$ ) ion with three strongly hydrogen-bonded ligand  $\text{H}_2\text{O}$  molecules, or a  $\text{H}_5\text{O}_2^+$  complex in which the proton is shared by two O atoms. Both structures could be identified in the simulation. Closer analysis revealed that these two solvation modes are closely related. Rapid proton transfers (on the scale of the vibrational motion of O atoms) continuously interconvert the structures and it is more appropriate to consider them as part of the same fluctuating complex. Proton transport could also be understood in terms of the structure of this complex and the fluctuations of the number of hydrogen bonds formed with the surrounding solvent [22].

In the simulation of proton solvation in reference [22] the counter-ion was omitted. This essentially imposed a fixed pH value. The equilibrium value of pH is, of course, a vital property of acidic solutions, and the determination of this number is an important step toward the validation of *ab initio* MD for aqueous chemistry. This was the main objective of a recent investigation of dilute sulphuric acid [23]. In the minimum-size model of a 5% concentration solution, a single  $\text{H}_2\text{SO}_4$  and 19  $\text{H}_2\text{O}$  molecules in a periodic cell, the dynamics was followed over 6 ps in order to evaluate the average number of protons  $n$  transferred to the solvent. Disregarding  $\text{H}_3\text{O}^+$ ,  $\text{HSO}_4^-$  contact ion pairs (and similar but rare combinations with  $\text{SO}_4^{2-}$ ), this number was found to be  $n = 0.6$ , which yields a pH of  $-0.2$ . Increasing the number of solvent molecules to 39, i.e. at half the previous concentration, and repeating the same analysis a substantial smaller value of  $n = 0.3$  was found, corresponding to a pH of 0.5. The pH for the larger system, although somewhat low, is of the correct order of magnitude. In the smaller system the pH is clearly too low. Part of the reason for this underestimation are the ambiguities in defining the number of protons absorbed by the water, which must be substituted in the expression for the pH. Boundary effects, which are more severe in the smaller system, will also play a role. With these and other remaining problems solved, the prospects of a quantitative description of acidic solutions by *ab initio* MD seem good, which opens the way to many interesting applications in organic and inorganic aqueous chemistry.

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