

Final Report

Condensed Phase Molecular Dynamics: Clusters, Interfaces and the Bulk

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The main goal of the present research program was to gain insight in the molecular level mechanism of basic elementary events taking place in various condensed phase environments: in molecular clusters, on solvent/air interfaces and in bulk solvents. In particular, we launched systematic theoretical investigations using computer simulation techniques in combination with high level quantum chemical methods to characterize and understand the common, basic patterns of solvation dynamics. The present research proposal was strongly connected to our previous successfully executed grants (K49715 and K75285), and can be viewed as their natural extension. There the focus was mainly on simulating and understanding the physical properties of excess electrons solvated in polar solvents, mainly in water. The physics of the hydrated electron system has important practical and theoretical implications in wide research areas. This is the reason why we still planned to invest significant research efforts in this subject. In addition, the ongoing scientific activity on the field gives us continuous ammunition and provokes us for further examinations. And although our original purpose was to extend our investigations to systems of increasing complexity using molecular solutes, the main avenue of the present research remained focused around the solvated electron with the extension of our investigated systems to non-aqueous environments (methanol and ammonia) and gradually shifting the simulation method from one-electron quantum dynamics to many-electron ab initio molecular dynamics (AIMD) techniques. The detailed explanation will be given below.

The first group of investigations aimed methodical problems. The first such problem we considered is the development of a new electron - water molecule pseudopotential for the hydrated electron system. This pseudopotential is a key element of the one-electron mixed quantum-classical molecular dynamics (QCMD) techniques that have been used in excess electron simulations for the last thirty years. It is clear that the use of one-electron QCMD simulations, although they are very approximative, is still unavoidable for large hydrated electron systems and/or for problems that require extensive samplings. This fact gives strong enough rationale for the development of a reliable new interaction model. For the classical

part of the pseudopotential, for the water model, we chose the polarizable Baranyai-Kiss water potential, since this potential reproduces the phase diagram of water extremely well, and describes the energetics of small water clusters semi-quantitatively. As the most important technical step, we successfully implemented a one-electron QCMD procedure for the hydrated electron in the classical molecular dynamics code of the Baranyai-Kiss water model. Then, we suggested the following protocol for the potential development procedure: a) Perform one-electron QCMD simulation for large water cluster anions (using some reasonable non-polarizable pseudopotential model), collect several snapshots of the cluster configurations. b) Cut out the nearest n molecules ($n = 2-36$) around the localized electron from each configurations, thus forming small water clusters. c) Perform reasonably high-level ab initio calculations and compute the vertical detachment energy (VDE) of the excess electron in each of these clusters. d) Minimize the squared difference of the ab initio VDE and the pseudopotential predicted VDE by optimizing the parameters of the pseudopotential. e) Perform another set of QCMD simulations using the optimized potential and analyze the results. Unfortunately, our efforts have not worked yet. This means that we have not been able to produce satisfactory agreement between ab initio and pseudopotential calculations. The main challenge we face here is the problem of a small number of configurations where huge deviations appear even after the most careful optimization procedure. Nevertheless, we analyzed several such critical configurations, observed several interesting trends in them, and now are collecting our most important conclusions in a manuscript that is in preparation.¹

As another important side product of our efforts in pseudopotential theory, we examined and analyzed a pseudopotential that predicts a non-cavity hydrated electron structure in the bulk (Larsen-Glover-Schwartz potential, LGS) and a potential that predicts a cavity structure (Turi-Borgis potential, TB). Our analysis was based on a) simple quantum mechanical model calculations, b) one-electron mixed quantum-classical molecular dynamics simulations of an excess electron in size selected water cluster anions, and c) ab initio calculations on small water cluster anions. We found that the LGS potential and a modified version of the LGS potential provide results that are inconsistent with the cluster size dependence of the experimentally observed data on these clusters. In particular, LGS simulations fail to reproduce the trends of the radius of the excess electron and the position of the absorption spectra with cluster size in water cluster anions. The simulated TB tendencies are qualitatively correct. In conclusion, we observe that the cavity preferring pseudopotential model (TB) results physical properties in significantly better agreement with experimental data than the models predicting non-cavity structure (LGS model) for the hydrated electron.

anions has been published in the Journal of Chemical Physics.⁴ We also investigated the molecular details following the photoexcitation of various size ground state equilibrated water cluster anions, but have not published the results separately yet. We plan to do that in the near future. Nevertheless, the conclusions of the study has been used in the subject below.

In our next, strongly related study, we focused on the non-adiabatic electronic relaxation following excitation of the ground state excess electron to its first excited state. We computed the excited state lifetime of the excess electron in various size water cluster anions using a quantized time correlation function based method. The results very nicely reproduce experimental data and are in complete agreement with our previous assignment on the structure of water cluster anions. We confirmed that the smallest clusters bind the electron on the cluster surface, and internalization of the electron becomes possible only for very large clusters (approximately $n > 500$). The research has a long history, since we started the project in 2013, and publication of the results came only in 2017. The reason for this delay is that our conclusions are not fully consistent with the interpretation of the leading experimentalists on the field. Our first attempt to publish these results in *Science* (after a significant debate) was not successful in 2014. However, later experimental results also questioned the original experimental interpretation, and illustrated the difficulty to explain these ultrafast experimental signals. Now, once again, publication of our simulations became feasible, and our paper appeared in the Journal of Physical Chemistry Letters.⁵

We note here that we also planned to perform free energy calculations on water cluster anions examining the electron transfer of the excess electron from the interior of the cluster to a surface state. Although we have computed the free energy profile using the TB potential, we feel that the employed model is too approximative to draw solid conclusions from these results. It would be more reliable to examine and interpret the free energy profile using a better performing pseudopotential, such as we planned to develop in the present research plan. We concluded that we have to repeat our simulations with the new pseudopotential model.

According to our original plans the third group of our investigations would have been devoted to the extension of our studies to more complex systems. Since we basically abandoned the development of a combined classical-quantum DFT approach, these type of studies remained to be performed in the future. As for the extension of the hydrated/solvated electron subject, here we also planned the investigation of more complex solutes using ab initio molecular dynamics methods. As an example, we proposed the investigation of the dynamics of the electron detachment reaction from an iodide ion in methanol using ab initio molecular dynamics methods. As an introductory study we wanted to test which quantum

chemistry methods can be applied for negatively charged methanol systems, the end product of the electron detachment from an iodide ion in methanol. In the first step we examined the physical properties of excess electrons in small methanol clusters and carried out a set of benchmarking calculations that were designed to evaluate the applicability of various level quantum chemical methods for methanol cluster anions. We found that of the presently used DFT based methods, the long range corrected BLYP functional may be the best choice in extensive quantum dynamics simulations for methanol cluster anions. We published these results in the *Journal of Chemical Physics*.⁶ In the second step, we have also started all-electron simulations on neutral methanol clusters, methanol cluster anions, and also modeled electron attachment to neutral clusters. The aim here is to re-evaluate our previous results based on one-electron QCMD simulations. Although, we expected to publish the results of this subject in 2016, we ran in unexpected technical difficulties. Due to the very weak electron binding nature of neutral methanol clusters, the realistic description of the diffuse excess electron distribution is a very challenging task in many electron cluster simulations. We, however, took an alternative route, and added an extra electron to cluster configurations with a pre-formed cavity that could initially bind the electron. Now the question we want to address is whether the initially well localized electron remains in the interior or diffuses to the surface during its relaxation. The work on this subject is in progress, and we hope to publish our results soon.⁷ We also started to carry out our research plan on the photoexcitation of the methanol - iodide system. We are currently testing the time-dependent DFT approach for the excited state dynamics of the photoexcited iodide ion in methanol (and also in water) bath.

As a further extension of our work, we have initiated a project for ammonia cluster anions, similar to that outlined above for the solvated electron system in methanol. Benchmark calculations on the vertical detachment energy were executed on small linearly hydrogen-bonded ammonia clusters of $n = 2 - 6$ monomer units. Our further work aims finding larger non-linear ammonia clusters that are able to bind an excess electron. These clusters would bridge the smallest clusters to those detected experimentally. A B.Sc. student prepared his thesis using these results.⁸ A manuscript on this topic is in preparation for publication.⁹

In summary, this was a very difficult and hectic research period with some very nice results and some deeply disappointing findings. All in all we published five papers in international journals, and have been left with a huge amount of tasks to finish. Nevertheless, I would like to indicate that three of the five papers are single authored by the PI. Also, the cumulative impact factor of the five papers exceeds 23, the impact factor of about eight

articles in such a good journal as the Journal of Chemical Physics. The greatest disappointment of the project is the failure (or rather delay) to finish the development of the electron-water molecule pseudopotential, because consequently several other important topics (among them the construction of the free energy profiles for water cluster anions) suffered delays. We have done a significant amount of work whose results are not published yet. We have at least three manuscripts in preparation, which we want to publish very soon, but within the next year. With these papers finished we would reach the 7-10 publication prognosis we made in the research proposal. I would like to emphasize that we intend to attach these publications to our final report within a year, an act that is, in our best knowledge, is allowed and supported in the NKFI regulations.

Here I think I cannot finish the report without mentioning the disappointing environment that has surrounded scientific research during the present research period. Firstly, it has been incredibly difficult to hire suitable research fellows for the present research tasks. The main reason is that most of the best students, young researchers, young talents leave the country and try to develop themselves in countries that appreciate and support scientific research (and, in general, knowledge) in a much higher level. The salary one can pay from a research grant like the present one is simply not motivating enough for highly educated researchers. Unfortunately, the two research fellows I was able to hire were just not motivated enough to do research independently. Secondly, unnecessary and sometimes surreal bureaucratic regulations concerning procurement of supplies (office supplies, computers and computer parts), travels to international meetings, service of goods etc. hinder the research seriously, and sometimes make productive scientific work absolutely impossible.

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