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Quantum simulation of hydrated electrons

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Abstract. A very short review is given of the methods and models applied in the numerical simulation of hydrated electrons. The results for the energetics, the diffusion and the transient dynamics are compared with experimental data. While there is good qualitative agreement, the quantitative discrepancies are still serious. One of the several effects, which are treated only in an approximate way in most calculations, is considered more closely, namely the coupling to the collective induced polarization of the solvent. We will present new results for the structure and energy, indicating that a self-consistent treatment of electronic polarization is important but is not likely to resolve the discrepancy with experiment.

1. Introduction

The continued interest in the hydrated electron is motivated by its importance both for the development of theory and the interpretation of experimental results (for references to experimental work see [1], for a fairly complete list of references to theoretical work and simulation see [2, 3]). The solvated electron can be considered as an elementary example of a quantum system in a localized state, for which the localization crucially depends on the coupling between thermal fluctuations with a finite lifetime in a disordered classical medium. This explains why computer simulation is an important and almost indispensable tool for the understanding of excess electrons in liquids. Another problem which gives the solvated electron its special position as a model system in theoretical physical chemistry is the interaction of such an electron with a closed shell molecule. A realistic model describing this interaction would be very useful in the study of chemical reactions in solution, since it would enable us to separate the chemically active part of the system from the inert solvent particles, for which the electronic structure would not need to be treated explicitly.

The hydrated electron has also made its appearance as an experimental tool in the study of the dynamics of polar liquids. The absorption spectrum in the range of 10 000 to 20 000 wavenumbers makes it, in combination with femtosecond laser pulse techniques [4, 5], a very sensitive probe of the fluctuations, which are responsible for solvation of charged solutes. One of the tasks of computer simulation is, therefore, to explain the excitation spectrum in equilibrium as well as in transient states. Another important experimental property, which computer simulation ultimately must be able to reproduce, is the diffusion coefficient.

In the first part of this contribution we give a quick evaluation of the progress that has been made towards achieving these goals. The conclusion of this survey is that, while simulation seems to account for the basic process of localization by solvation, many

serious discrepancies between simulation and experiment remain. For dynamical properties, this is most likely due to limitations of the current simulation methods. For static properties, such as the absorption spectrum, these methods can be considered adequate and here the interaction models, which have been employed so far, are most likely at fault. In the second part we single out one particular element of the electron solvent interaction for closer study, namely the coupling of the solvent to the collective electronic polarization.

2. Methods and models

The first computer simulation studies of excess electrons in liquids were performed by means of the path integral method (see e.g. [2]). In this approach a single quantum particle is represented by a set of classical pseudo particles interacting with each other and the classical solvent. The major advantage of the path integral method is that it allows for a finite temperature of the quantum particle. The drawback is that the correspondence to a classical many body system is only valid for static averages like structure and energetics, not for dynamics. The path integral calculations established that, in equilibrium, the electron is bound in a cavity in the liquid and is solvated very much like a classical anion such as Cl^- [6, 7]. The cavity state is strongly ground state dominated, the energy gap to the first excited state being at least 1.5 eV.

This observation led to the development of simulation techniques that couple the instantaneous ground state wavefunction to the motion of the solvent and, therefore, enable us to investigate the adiabatic dynamics defined by the lowest Born–Oppenheimer surface. In the most popular adiabatic molecular dynamics technique the wavefunction is expanded in plane waves [2, 8, 9]. The adiabatic ground state at a given time step is obtained by projection from the ground state of the previous step using a relaxation method: the initial wavefunction is propagated in complex time with the solvent fixed in the instantaneous real time configuration. An alternative method uses a localized basis set of Gaussians rather than plane waves. The positions and widths of the Gaussians are optimized by a molecular dynamics algorithm which treats these parameters as classical variables similar to the pseudo particles in the path integral method [10].

The effective interaction of an electron with a solvent molecule can be resolved into four contributions [6, 7]: the electrostatic interaction, a short range repulsion, the monopole induced dipole coupling and exchange correlation effects. The electrostatic part arises from the Coulomb interaction with the fixed molecular charge distribution which, as it turns out, can be represented quite accurately by the point charge sites used in the model for the solvent–solvent interaction. The repulsion is a consequence of the Pauli principle, which requires that the wavefunction of the excess electron be orthogonal to the molecular orbitals. This term is given by one or more exponents centred on the atomic sites. The polarization is usually accounted for in the two-body approximation, i.e. as a r^{-4} dependence with some form of damping at small distance. Several models have been proposed with various degrees of sophistication. The most elementary, the so-called primitive model, reduces the potential to the electrostatic term with a truncation of the attractive Coulomb interaction within a certain radius ($\sim 1 \text{ \AA}$) of the positive charge sites. The more detailed models also include orthogonalization repulsion and polarization.

3. Comparison with experiment

All the models agree on the basic picture of the cavity state. In fact, the results for structure are remarkably model independent. As an example, we give in figure 1 the

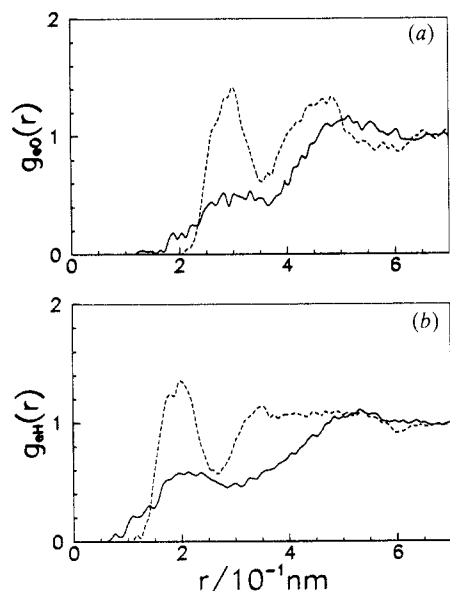


Figure 1. Radial distribution of oxygen sites (a) and hydrogen sites (b) with respect to the expectation value of the position of the electron. Shown are the results for the primitive model (broken curve) and the model that includes collective polarization effects in the solvent (full curve).

distribution of oxygen and hydrogen sites (broken curves) around the average position of the electron. These results were obtained using the primitive model and the adiabatic molecular dynamics technique based on an optimized Gaussian basis set [10]. The effective radius of the wavefunction for this case is 2.2 Å and the binding energy (the sum of the quantum kinetic and potential energies) is 2.25 eV. The exact values for the more detailed models can be found in the original papers [2, 6, 7]. None of these quantities, however, can be directly observed by experiment in the liquid. The one static property for which the prediction made by a simulation is comparable to the experimental value is the position and width of the peak in the light absorption spectrum. Experimentally the maximum is located at 1.75 eV, while the models described above all find approximately the same value of 2.3 eV [7, 8]. This blue shift proves difficult to correct: modifying the interaction potential in order to reduce the excitation energy invariably leads to an increase in the cavity size and an unacceptable loss in binding.

A parameter that can be used to test the dynamics of the simulation is the diffusion coefficient. Experimentally, the diffusion coefficient of the electron in both water and ammonia is found to be two to three times greater than the self-diffusion coefficient of the solvent. In adiabatic dynamics calculations the electron moves at virtually the same rate as the solvent molecules [10, 11]. Recently, experimental data on transient effects during the solvation of an injected electron have also become available. These data suggest a two-state picture in which the electron first settles into an excited state that is already solvated to a considerable degree and then decays to the ground state. The characteristic time for both processes is in the order of a few hundred femtoseconds. In simulation, on the other hand, solvation in a ground state is almost immediate, on a time scale of a few tens of femtoseconds [3].

The adiabatic nature of the simulation methods is, of course, an obvious limitation, which may well imply that these techniques are not very relevant to the understanding of the relaxation dynamics. In fact, very recent simulation studies of the transient dynamics, which include non-adiabaticity to some extent, support the two-state picture

[12]. However, it is felt that the adiabatic technique is adequate for static properties and that the blue shift in the absorption spectrum cannot be attributed to non-adiabatic effects alone.

4. Solvent polarization coupling

The models of the type discussed above all treat the polarization term in the two-body approximation. However, in the bulk solvent the induced dipoles influence each other. In [7] it was shown that if the dipoles created by the presence of the excess electron (see also [2]) are allowed to interact, the maximum of the absorption spectrum shifts to lower frequencies. However, polarization by the permanent charges in the solvent was not taken into account in this calculation. We have investigated the effect of this inconsistency by replacing the mean field model for the water used in [7] with the polarizable model that we have recently developed [13]. In our approach the polarization is described by the dipole moment of four closely spaced charge sites. The location of the sites is held fixed in the molecular frame, while their charge fluctuates in response to the local Coulomb potential. A short-range damping is introduced by distributing a fluctuating charge over a Gaussian with a finite width. This representation of the induction is particularly convenient when applied with our adiabatic dynamics algorithm for the solvated electron, which is also based on Gaussians (details can be found in [10, 13]).

If we take the exclusion interaction from [7] and the electrostatics as outlined above, we find a substantially increased cavity size. From the distribution of hydrogen and oxygen sites shown in figure 1 it can be seen that the first solvation shell has become rather diffuse and clear coordination is lost. The increase of the effective width of the wavefunction to 2.6 Å does yield the desired reduction of the excitation energy to 1.7 eV. However, this is at the expense of a large amount of binding energy which is reduced to 1.1 eV (for a sample of 215 solvent molecules) and, as a result, the enthalpy of solvation, which includes the reorganization energy of the water, is positive. This is clearly not realistic. We conclude, therefore, that the coupling to the collective polarization, at least in our model, does not resolve the problem of the blue shift of the calculated spectrum with respect to the measured one.

References

- [1] Hart E J and Anbar M 1970 *The Hydrated Electron* (New York: Wiley)
- [2] Coker D F and Berne B J *Excess Electrons in Dielectric Media* ed J-P Jay-Gerlin and Ferradini C (Boca Raton, FL: Chemical Rubber Company Uniscience Press)
- [3] Rosicky P J and Schnitker J 1988 *J. Phys. Chem.* **92** 4277
- [4] Migus A, Gauduel Y, Martin J L and Antonetti A 1987 *Phys. Rev. Lett.* **58** 1559
- [5] Long F H, Lu H and Eisenthal K B 1990 *Phys. Rev. Lett.* **64** 1469
- [6] Schnitker J and Rosicky P J 1987 *J. Chem. Phys.* **86** 3462, 3471
- [7] Wallqvist A, Thirumalai D and Berne B J 1987 *J. Chem. Phys.* **86** 6404
- [8] Schnitker J, Motakabir K, Rosicky P J and Friesner R 1988 *Phys. Rev. Lett.* **60** 456
- [9] Barnett R B, Landman U and Nitzan A 1989 *J. Chem. Phys.* **90** 4413
- [10] Sprik M and Klein M L 1989 *J. Chem. Phys.* **91** 5665
- [11] Schnitker J and Rosicky P J 1989 *J. Phys. Chem.* **93** 6965
- [12] Rosicky P J private communication
- [13] Sprik M and Klein M L 1988 *J. Chem. Phys.* **89** 7556