



## Light metal ions in water: Quantal and classical simulations for ${}^7\text{Li}^+$ .

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### Abstract

Path integral Monte Carlo computations have been done to study the local structure of water molecules around an isolated lithium ion ( ${}^7\text{Li}^+$ ) at  $T=298\text{K}$ . The solute was treated as a quantal particle and the water solvent was treated classically. The water-water interaction was modelled by the MCY pair-potential and the solute-water interaction by the Kistenmacher *et al.* pair-potential. Purely classical simulations, at the same conditions and using the same model potentials, were also performed for comparison.

Significant changes are observed on the results of the quantal simulations when compared with the results of the classical simulation. The major difference is the coordination number that increases from 5, the result of the classical simulation, to 6, for the quantal simulation. In addition, structural analysis of the generated configurations showed that the local structure of the water molecules surrounding the ion is also clearly different in the two simulations. The reliability of the results is discussed.

### 1. Introduction

The study of ionic solutions is fundamental to the understanding of their role in many chemical and biophysical processes. To date, numerous experimental and theoretical investigations have dealt with this subject [1-5]. Among the theoretical work, statistical simulations that gave significant contributions to our understanding of these systems should be singled out [3-5].

Most of the simulation work so far have been focused on developing and testing accurate interaction potentials. Attempts, have been made to design potentials that take into account the important many-body effects [5] to best reproduce the experimental data. However, apart from the quality of the potentials to be used, there are other effects that can affect the results of the simulations. In the case of light solvated solutes, their quantum properties may have some

influence on the local structure of the water molecules in the solution. In the last few years, quantum solvated particles, like the solvated electron, muonium or hydrogen, have already been studied with path integral methods [6,7]. The extent of the quantum effects on a given particle is directly connected with its degree of localization. This can be inferred from the thermal de Broglie wavelength  $\lambda=(h^2/mkT)^{1/2}$  of the particle. If the potential energy of the particle does not change appreciably over distances of the order of  $\lambda$  then the system may be treated classically. When this condition is not satisfied, then a quantum description is strictly necessary.

Most of the solvated particles studied until now are very light, and they are expected to have strong quantal properties. Other more massive particles have been studied, mainly in the condensed phase [8,9]. The lightest metal ion is the  $\text{Li}^+$  ion and its thermal wavelength  $\lambda$  (isotope  $^7\text{Li}$ ) is  $0.152\text{\AA}$  (at 298K) to be compared with  $1.95\text{\AA}$ , the typically Li-oxygen distance ( $d$ ) in water. Since this  $\lambda$  value is reasonably smaller than  $d$ , the particle should be localized. However, due to the steepness of the  $\text{Li}^+$ -water potential, reasonable variations on the potential energy can be expected on a  $\lambda$  length scale. Quantum effects for this particle may thus be expected. The main purpose of this work is the investigation of this possibility.

In this work, the water has been treated classically, which is reasonable for its translational degrees of freedom [9]. On the other hand, quantum effects are more important for the orientational degrees of freedom of water which, for a complete description, should be taken into account. However, apart from being extremely demanding computationally, their effect appear to be small [9,10] and thus the present work is done at this much less expensive level of calculation. The outline of the paper is as follows. In section 2 below, the methodology used to treat the quantum solute and the details of the Monte Carlo (MC) simulations are presented. The results of these simulations are collected in section 3. Finally, the main results of this work are summarized in section 4.

## 2. Methodology

### 2.1. Simulations of a quantum solute

Water is treated as a classical rigid body and the lithium ion as a quantum particle. For modelling the quantum particle we adopted the Feynman path integral representation [11]. In this representation the quantum particle is mapped onto a cyclic chain of  $P$  pseudo-classical particles (beads), this isomorphism being exact in the  $P \rightarrow \infty$  limit. In the cyclic chain, each bead  $i$  interacts with its neighbours  $i-1$  and  $i+1$  through an harmonic potential with force constant  $mP/2h^2\beta^2$ , where  $m$  denotes the particle mass,  $h$  is the Planck's constant divided by  $2\pi$  and  $\beta=1/kT$ ,  $k$  being the Boltzmann's constant and  $T$  the absolute temperature. Note that this harmonic potential derives from the kinetic energy operator of the quantum particle. Each bead is also acted on by the external interaction potential, divided by  $P$ . So, with a Feynman  $P$ -point discretization for the quantum particle and the  $N$  classical water molecules we have a "potential" like:

$$\Phi = \sum_{i>j}^N V(R_i\Omega_i, R_j\Omega_j) + 1/P \sum_{i=1}^N \sum_{j=1}^P U(R_i\Omega_i, r_j) + mP/2h^2\beta^2 \sum_{i=1}^P (r_i - r_{i+1})^2 \quad (r_{P+1}=r_1) \quad [1]$$

where  $R_i\Omega_i$  denotes the center of mass and orientation, respectively, of the  $i$ th water molecule and  $r_i$  represents the coordinates of the  $i$ th bead of the lithium necklace.  $V(R_i\Omega_i, R_j\Omega_j)$  gives the potential between the  $i$ th and  $j$ th water molecules and  $U(R_i\Omega_i, r_j)/P$  gives the potential between the  $i$ th water molecule and the discrete ion bead  $j$ ,  $U(R\Omega, r)$  being the potential of interaction of one water molecule with one classical lithium ion at position  $r$ . Making  $P=1$ , the cyclic chain "polymer" reduces to one bead, the harmonic term vanishes and the potential  $\Phi$  reduces to that corresponding to  $N$  classical water molecules interacting with each other and with one classical ion.

This "potential" function looks like a classical "potential" of one cyclic-chain polymer with harmonic interactions between the nearest neighbours, interacting with a collection of  $N$  molecules. The

"polymer" represents the quantum particle and, in the case of several quantum particles interacting with each other, one would have in this picture, several "polymers" interacting. There are, however, substantial differences between these "polymers" and true polymers. In fact, the beads of these "pseudo"-polymers carry labels and different polymers interact with each other through beads with the same labels. Another difference is that the minimum energy distance between beads of the same "polymer" is zero. The strength of the harmonic interactions depends on the mass of the particle, the temperature and the number of "particles" in the polymer. It is clear that heavy particles will tend to coalesce on a point in contrast with light particles which will spread over larger regions of space. So, the "potential" in eq. [1] can be seen as the classical limit of the  $N$  massive particles in which all the beads had coalesced to the same point, maintaining the quantum features of the light particle.

With this "potential" a stochastic simulation with the Metropolis recipe [12] can be performed to get observable averages or, if masses and momenta conjugated to the configurational variables are introduced, it is possible to do molecular dynamics simulations. It must be stressed that the dynamics obtained does not correspond to the real dynamics of the system, so that, one is limited to the calculation of static quantities.

## 2.2. Details of the simulations

The MC simulations have been carried out on the NVT ensemble at a temperature of 298K for the diluted solution of  ${}^7\text{Li}^+$ , represented by the system  $\text{Li}^+(\text{H}_2\text{O})_{200}$ . In these simulations, a cubic box of side length of about  $18\text{\AA}$  has been chosen to give a density of *ca.*  $1\text{gcm}^{-3}$  for the 200 water molecules. The simulations have been done according to the Metropolis algorithm [12] and periodic boundary conditions under the minimal image convention [13] were applied. The intermolecular interactions have been computed under the assumption of pairwise additivity. For the water-water interactions, the *ab initio* MCY potential [14] was used. This potential is known to give a reasonable description of water in the condensed phase [15]. For the ion-water interactions the "simple" model potential of Kistenmacher *et al.* [16] was used, which is also based on *ab initio* computations. These two potentials were chosen in order to have the same kind of potentials, i.e., potentials entirely derived from *ab initio* computations and not empirical ones that are normally forged to reproduce experimental results.

All the simulations started with a initial configuration that has been obtained from a cubic lattice of H<sub>2</sub>O molecules.

In the purely classical simulations, the number of steps needed to achieve statistical equilibration was  $2 \times 10^4$  and another  $2 \times 10^4$  MC steps were used for data collection (An MC step is made up of 200 single water sequential steps. Notice that the ion was also moved periodically.)

The quantal simulations were tested with increasing number of beads (10, 20 and 30) until the results of the simulations did not show significant difference within the statistical errors. This number was then fixed at 20 which appears to be enough. For each simulation we took  $2 \times 10^4$  MC steps (for each moved water, one bead was also moved) to equilibrate the entire system and  $2 \times 10^4$  more steps to collect results. It should be stressed that these simulations were very hard to equilibrate since one is dealing with a stiff "polymer" chain that may relax very slowly, and thus several test runs were made with longer periods to assure that no further drift of the properties occurred. On the other hand, to speed up the convergence of the quantal simulations, apart from one bead movements, periodic translations of the entire necklace were also done. In fact, this strategy was shown to really decrease the needed computation time. The averages were taken as block averages with size of 250 MC steps and then checked for the degree of correlation. Successive sets of these blocks were combined until no correlation appeared between the averages, their final errors being estimated from their standard deviations.

In all the simulations, the structure of the solution was analysed in terms of radial distribution functions (RDFs) and coordination numbers. In addition, a pattern recognition analysis of the significant structures of the Li<sup>+</sup> solution has been performed for both simulations, using the method developed by Tapia and Lluch [17]. This method allowed us to clarify the geometrical disposition of the H<sub>2</sub>O molecules of the first Li<sup>+</sup> shell.

An important quantity to discuss the quantum particle is the average value

$$R = \left( P / (P-1) \sum_{i=1}^P \langle (r_i - r_{i+1})^2 \rangle \right)^{1/2} \quad (r_{P+1} = r_1) \quad [2]$$

which is related to the thermal de Broglie wavelength by

$$\lambda = R / \sqrt{3} \quad [3]$$

Thus, computing  $\lambda$  as above for the quantum solute in the presence of water and by comparing it with the free particle value, it is possible to estimate the degree of dispersion of the quantum particle.

### 3. Results and discussion

The main results of the classical and quantal simulations are presented in table I.

Table I - Li<sup>+</sup>- water first coordination shell data.

Method	a	a	b	b
	R <sub>LiO</sub> [Å]	R <sub>LiH</sub> [Å]	n <sub>O</sub> [Å]	n <sub>H</sub> [Å]
MC, Classical	1.98	2.55	5.0	10.7
MC, Quantal	2.03	2.59	6.0	12.7
Exper. <sup>c</sup>	1.95	2.31-2.55	2.3-5.5	-----

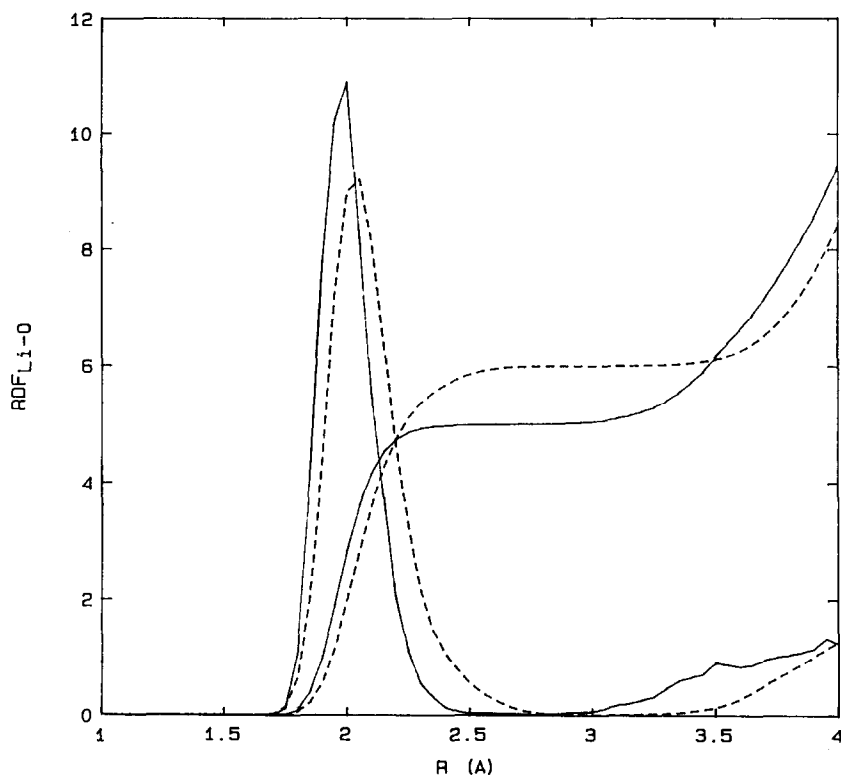
<sup>a</sup> Position of the maxima on the first peaks of the radial ion-oxygen (R<sub>LiO</sub>) and ion-hydrogen (R<sub>LiH</sub>) distribution functions.

<sup>b</sup> Calculated by integrating the radial ion-oxygen distribution function (n<sub>O</sub>) or the radial ion-hydrogen distribution function (n<sub>H</sub>) up to their first peak minima.

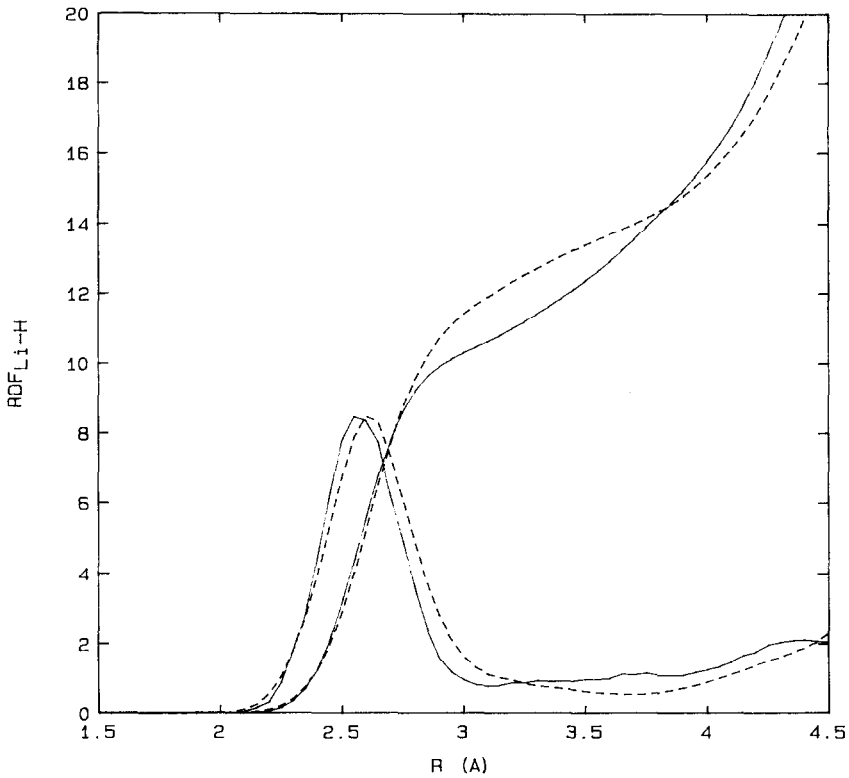
<sup>c</sup> The range of experimental results shown were obtained for 27.77, 9.95 and 3.57 molal solutions of LiCl [12].

A selection of experimental results is also presented in this table for comparison. The classical results for the position of the first maxima of the ion-oxygen and ion-hydrogen RDFs do agree with those obtained on the experimental work [2]. In the quantal simulation, these peaks are slightly shifted outwards. Looking at the experimental data in table I, it is clear that the hydration of  $\text{Li}^+$  is markedly influenced by the concentration of the solution, the coordination number decreasing as the concentration of the sample solution increases [2]. Experimental results for the lowest concentration give a coordination number of 5.5 which is in fair agreement with both, classical and quantal predictions.

A better insight into the differences between the distribution functions determined in the purely classical and the quantal simulation is gained from Fig. 1.



**Fig. 1 a** - Ion-oxygen radial distribution function and its corresponding running coordination number for the quantum (dashed line) and classical (solid line) simulations of a diluted  $\text{Li}^+$  solution at 298K.

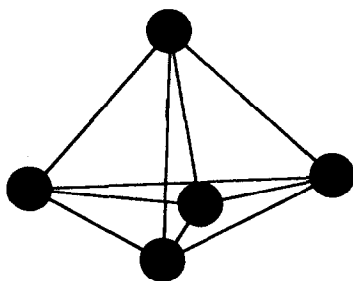


**Fig. 1 b** - Ion-hydrogen radial distribution function and its corresponding running coordination number for the quantum (dashed line) and classical (solid line) simulations of a diluted  $\text{Li}^+$  solution at 298K.

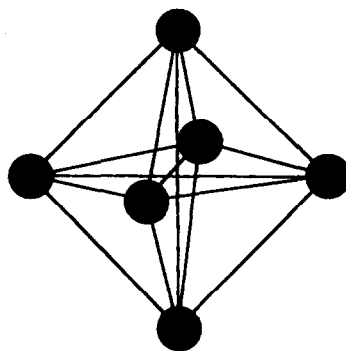
It is clear that the quantal RDFs do have a broader first solvation shell and that they extend to longer radial distances. In a finer observation the quantal RDFs are seen to start before than their classical counterparts, even if their maxima and minima are shifted outwards. This being certainly related to a quantum tunneling effect. It can also be seen in Fig. 1 that the quantal RDFs are more structured than their classical counterparts.



For both simulations, the generated equilibrium configurations have been analysed by the pattern recognition method referred in section 2.3. The generated equilibrium configurations were first sorted into groups in such a way that only the water molecules falling inside the first shell were considered. In particular, this analysis showed that, in a sphere of radius  $R_{\text{LiO}}=3\text{\AA}$  centered in the ion for the classical case (or in the barycenter of the necklace for the quantum case), 96% of the equilibrium configurations had 5 water molecules (or 98% of the equilibrium configurations had 6 water molecules on the quantal simulations). The resulting groups were then divided into classes using a geometrical criterion which is based on the oxygen-oxygen inter configuration distances (see Ref. [18] for details on this classification). The structures of the most populated classes found in this way for the  $\text{Li}^+$  first shell are depicted for the classical and quantal simulations in Fig. 2a and Fig.2b, respectively.



**Fig 2 a** - Sketch of the most significant structure of the  $\text{Li}^+ - (\text{H}_2\text{O})_{200}$  first hydration shell determined in the classical simulation at  $T=298\text{K}$ .



**Fig 2 b** - Sketch of the most significant structure of the  $\text{Li}^+ - (\text{H}_2\text{O})_{200}$  first hydration shell determined in the quantal simulation at  $T=298\text{K}$ .

Fig 2a shows a (unsymetric) distribution of five water molecules located over a sphere centered at the metal ion with a radius (Li-O distance) of  $2.02\pm 0.06\text{\AA}$ . Although slight distortions are seen in Fig. 2b, it is clear that the arrangement of the oxygen sites in the quantal hydration complex is octahedral.

Table II shows the energy averages for the two simulations, together with the values of R as defined by eq. [2], obtained for the quantal solute.

**Table II -** Classical and quantal MC results of  $\text{Li}^+ - (\text{H}_2\text{O})_{200}$  system at 298K.

Method	a $E_{i,w}$ [kJ/mol]	b R [Å]
MC, Classical	-1117±7	————
MC, Quantal	-1148±14	0.250±0.002

**a**

Energy for the ion-water interactions.

**b**

Computed using eq. [2] of section 2.2.

The classical results for the ion-water energy are in good agreement with other classical simulation results [3,4]; the quantal results, although affected by more important statistical errors (as the generated configurations are more strongly correlated than in the classical case - see table II), show a lower value for the energy which is not surprising since the metal ion is coordinated with one more water molecule.

More surprising is the result of R which is not very different from the free particle value (0.265Å) in spite of the presence of the water molecules. It seems that the quantum delocalization of the lithium ion pushes the water molecules away, and this may, in addition, allow the entrance of one more water molecule in the first coordination shell. An effect similar to this was also observed in the simulation of muonium in water by De Raedt *et al* [7].

#### 4. Conclusions

In this paper, simulations are presented for a diluted aqueous solution of  ${}^7\text{Li}^+$ , using a conventional classical Monte Carlo simulation, and a mixed quantum-classical Monte Carlo path integral simulation. Differences between the two approaches are found, especially different coordination numbers and non-zero probability for finding water molecules at shorter distances from the lithium ion in the quantal method. This latter effect, though rather faint, is worth noting as it may be linked to quantum tunneling.

The coordination number of 5 found in the classical method as been also obtained by other authors [3]. The present simulation was taken to a rather long 8 million configurations to assure good statistics and for better guarantee of the results. Tests were made with shorter runs, starting from a randomized configuration and from an octahedral shell. The results of these tests suggest the existence of a metastable octahedral configuration with a total energy slightly above that obtained here. It is interesting to note that the quantal simulations remained for a certain period in a configuration with a 5 water first shell, then migrating and staying indefinitely in the 6 water coordination result reported above. Such transition was not observed along the classical simulations.

Of course there is scope for improvement of this work. On the one hand, the comparison of these results with a full quantal simulation taking into account the quantum degrees of freedom of water would be interesting. On the other hand, this work is based on the use of simple two-body potentials and their improvement to include higher order terms may be worthwhile.

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