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The hydration shell structure of Li^+ investigated by Born–Oppenheimer ab initio QM/MM dynamics

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Abstract

A combined ab initio quantum mechanical (QM) and molecular mechanical (MM) molecular dynamics simulation has been applied to study the non-additive contributions to the surroundings of Li^+ in water. The first hydration sphere of Li^+ is treated by Born–Oppenheimer ab initio quantum mechanics, while the rest is described by classical pair potentials. A tetrahedral structure of four water molecules in the first solvation shell of Li^+ is found by this combined QM/MM method with a valence double-zeta basis set, in contrast to the octahedral structure obtained by the traditional simulation using pair potentials. © 1998 Elsevier Science B.V.

1. Introduction

In biology and medicine, lithium ions are well-known for widespread and diverse effects, both in animals and plants [1,2]. Even at low concentration, the biochemical and pharmacological activity of lithium is enormous. Consequently, a substantial number of experimental and theoretical investigations on the structural properties of hydrated Li^+ has been carried out. According to neutron diffraction, the hydration sphere of Li^+ consists of a varying number of water molecules depending on the Li^+ concentration, ranging from 6.5 at low concentrations to 3.2 in 14 molal [3,4] solution. Theoretical studies have also reported various coordination numbers of Li^+ , ranging from 3.9 to 6 [5–10].

The exact intermolecular interaction for an n -body system can be written as the sum of 2, 3, ..., up to n -body interactions. The convergence of the higher terms (3, 4, ..., n -body) is rather slow and the terms tend to have alternating signs [11]. It has been reported in many studies that non-additive contributions always play a significant role and are important to describe correctly the properties of strongly interacting systems [12–14]. The pair approximation for alkaline cation–water interactions typically yields an overestimation of interaction energy by about 10% in the corresponding complexes [11]. In the Li^+ –water system, the inclusion of 3-body interaction terms for the intermolecular interaction energies improves agreement with experimental observations [12]. The error of the pair approximation has been found to amount to 10–15%. The neglect of 3-body and higher terms favours wrong geometrical arrangements, especially in the first solvation shell of ions.

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The construction of analytical potential functions including higher terms, such as 3- [15] or 4-body terms [16], implies increasingly complicated calculations and fitting procedures and is, therefore, hardly feasible for larger systems. This problem can be overcome by combined quantum mechanical (QM) and molecular mechanical (MM) methods [17,18]. As the non-additive contributions in aqueous electrolyte solutions are of importance mainly for the first solvation shell, the system naturally can be partitioned into two parts: an inner region treated quantum mechanically and an outer region described by molecular mechanics. The forces arising within the inner region including the first hydration sphere of the ion can be calculated from electronic quantum mechanics and the remaining forces in the system (including the ones arising from interactions between molecules inside and outside the inner region) can be obtained by molecular mechanics force fields. The details of our method and some applications for condensed-phase systems are available in Kerdcharoen et al. [19] and Tongraar et al. [20]. In this work, our combined QM/MM method will be applied to investigate the importance of non-additive terms for the hydration of Li^+ .

2. Details of calculations

2.1. Evaluation of many-body interactions

The effect of non-additivity in ion–water systems is related to the strength of binding between the ion and water. Hence, this effect in the first solvation shell of singly charged ions like Li^+ is expected to be smaller than for multiple charged ions. In order to estimate the influence of many-body terms, energy

optimizations of $\text{Li}(\text{H}_2\text{O})_n^+$, $n = 1, 2, 3, 4$ and 6 , were carried out using a $\text{DZV} + \text{P}$ basis set for H_2O [21] and DZVP basis set for Li^+ [21]. Many-body interactions are defined as the difference of the total interaction energy and the energy calculated from the sum of all pair interactions. The total interaction energy of $\text{Li}(\text{H}_2\text{O})_n^+$ complexes can be computed using the supermolecular approach by:

$$\Delta E_{\text{ab}} = E(\text{Li}(\text{H}_2\text{O})_n^+) - E(\text{Li}^+) - nE(\text{H}_2\text{O}), \quad (1)$$

The sum of all pair interactions can be obtained by:

$$\begin{aligned} \Delta E_{\text{pair}} = & \sum_i^n [E(\text{Li}^+ - \text{H}_2\text{O}^i) - E(\text{Li}^+) - E(\text{H}_2\text{O})] \\ & + \sum_{j>i}^n [E(\text{H}_2\text{O}^i - \text{H}_2\text{O}^j) - 2E(\text{H}_2\text{O})]. \end{aligned} \quad (2)$$

Absolute and relative interaction energy differences, ΔE_{diff} and $\%E^{\text{nb}}_{\text{bd}}$ with respect to the pair potential can be calculated by:

$$\Delta E_{\text{diff}} = \Delta E_{\text{ab}} - \Delta E_{\text{pair}} \quad (3)$$

$$\%E^{\text{nb}}_{\text{bd}} = 100 \left(1 - \frac{\Delta E_{\text{ab}}}{\Delta E_{\text{pair}}} \right). \quad (4)$$

The results of geometry optimizations and the corresponding data for many-body effects are given in Table 1.

2.2. Molecular dynamics simulations

A flexible model for intermolecular [22] and intramolecular interactions [23] was employed for water. The pair potential function for Li^+ –water was newly constructed. 1800 Hartree–Fock interaction energy points obtained from GAUSSIAN94 [24] calculations using a $\text{DZV} + \text{P}$ basis set for H_2O [21] and a DZVP basis set for Li^+ [21] were fitted to the analytical form:

$$\begin{aligned} \Delta E_{\text{Li}^+ - \text{H}_2\text{O}} = & \sum_{i=1}^3 \frac{A_{ic}}{r_{ic}^4} + \frac{B_{ic}}{r_{ic}^5} + C_{ic} \exp(-D_{ic} r_{ic}) \\ & + \frac{q_i q_c}{r_{ic}}, \end{aligned} \quad (5)$$

Table 1
Optimized geometries and corresponding many-body effects in $\text{Li}(\text{H}_2\text{O})_n^+$ complexes

n	$r_{\text{Li}-\text{O}}$	$r_{\text{O}-\text{H}}$	\angle_{HOH}	ΔE_{ab}	ΔE_{pair}	ΔE_{diff}	$\%E$
1	1.87	0.95	106.3	-36.8	-36.8	-	-
2	1.89	0.95	106.6	-69.6	-71.5	1.9	2.7
3	1.93	0.95	106.9	-94.9	-103.8	8.8	8.5
4	2.05	0.94	105.8	-103.5	-114.0	10.4	9.1
6	2.15	0.94	107.8	-128.7	-160.3	31.6	19.7

Table 2

Optimized parameters of the analytical pair potential for the interaction of water with Li^+ (interaction energies in kcal mol^{-1} and distances in \AA)

Atom	q	A ($\text{kcal mol}^{-1} \text{\AA}^2$)	B ($\text{kcal mol}^{-1} \text{\AA}^5$)	C (kcal mol^{-1})	D (\AA^{-1})
O	-0.6598	-730.35028	618.63508	14685.929	3.4298689
H	0.3299	47.940713	-5.7743713	1.8334492	0.4253268

where A , B , C and D are the fitting parameters (see Table 2), r_{ic} denotes the distances between the Li^+ cation and the i th atom of water and q are the atomic net charges. Parts of the potential energy surface resulting from the fitted function are displayed in Fig. 1a,b. They correspond to movements of Li^+ around the water molecule. The function exhibits a stabilization energy of $-37.0 \text{ kcal mol}^{-1}$ at a Li^+ -O distance of 1.9 \AA in the direction of the dipole moment of water. This stabilization energy has to be compared with the experimental value of $-34 \text{ kcal mol}^{-1}$ in the work of Dzidic and Kebarle [25], who did not give error limits for the experimental heats of formation. However, the error and covariance of these experimental data should be in the range of ± 1 to $\pm 3 \text{ kcal mol}^{-1}$ [26]. Clementi et al. [26] showed that correlation effects are not an important contribution and are negligible for the interaction energy of Li^+ with a single water molecule.

A classical molecular dynamics simulation using pair potentials was performed first. Afterwards, a combined QM/MM molecular dynamics simulation was performed at the Hartree-Fock level using a valence double-zeta basis set (LANL2DZ basis set in GAUSSIAN94), starting from the previously obtained equilibrium configuration. The reaction-field procedure [27] was employed for the correct treatment of long-range interactions. The diameter of the first solvation shell of Li^+ , stemming from the pair potential simulation was selected as the size of the QM region. Both simulations were carried out in a canonical ensemble at 298 K with a time step of 0.2 fs. Assuming the density of pure water, a box length of 18.9 \AA results for one Li^+ in 199 water molecules. The classical molecular dynamics simulation started from a random configuration and was equilibrated for 20000 time steps. The simulation was continued for 60000 time steps to collect configurations every 10th step. The combined QM/MM molecular dy-

namics simulation started with a re-equilibration for 10000 time steps, followed by another 10000 time steps to collect configurations every 5th step. The quantum mechanical calculations and the simulations were performed on a SGI POWER CHALLENGE XL at the computing center, University of Innsbruck.

3. Results and discussion

3.1. Role of non-additive terms

As can be seen from Table 1, the significance of many-body interactions increases with the number of ligands in the first shell. The change in the Li^+ -O distance can be understood from ligand-ligand repulsion. The assumption of pairwise additivity leads to an error of 19.7% in the case of the octahedral complex $\text{Li}(\text{H}_2\text{O})_6^+$. From this value, it has to be expected that non-additive interactions play a significant role and are not negligible for the treatment of the first hydration shell of Li^+ .

3.2. Structural data

Fig. 2a,b shows the Li-O and Li-H radial distribution functions (RDF) and their corresponding integration numbers, comparing the results obtained from classical pair potentials and combined QM/MM simulations. The first Li-O maximum of the classical pair potentials simulation is centered at 2.06 \AA and the first solvation shell is completely separated from the second one, giving a coordination number of 6. The first Li-O peak observed in the QM/MM simulation occurs at a shorter distance (1.94 \AA) and the hydration shell structure seems to be less pronounced as can be seen from the decrease of the peak height. The first solvation shell is not clearly separated from the second one. Integration yields an

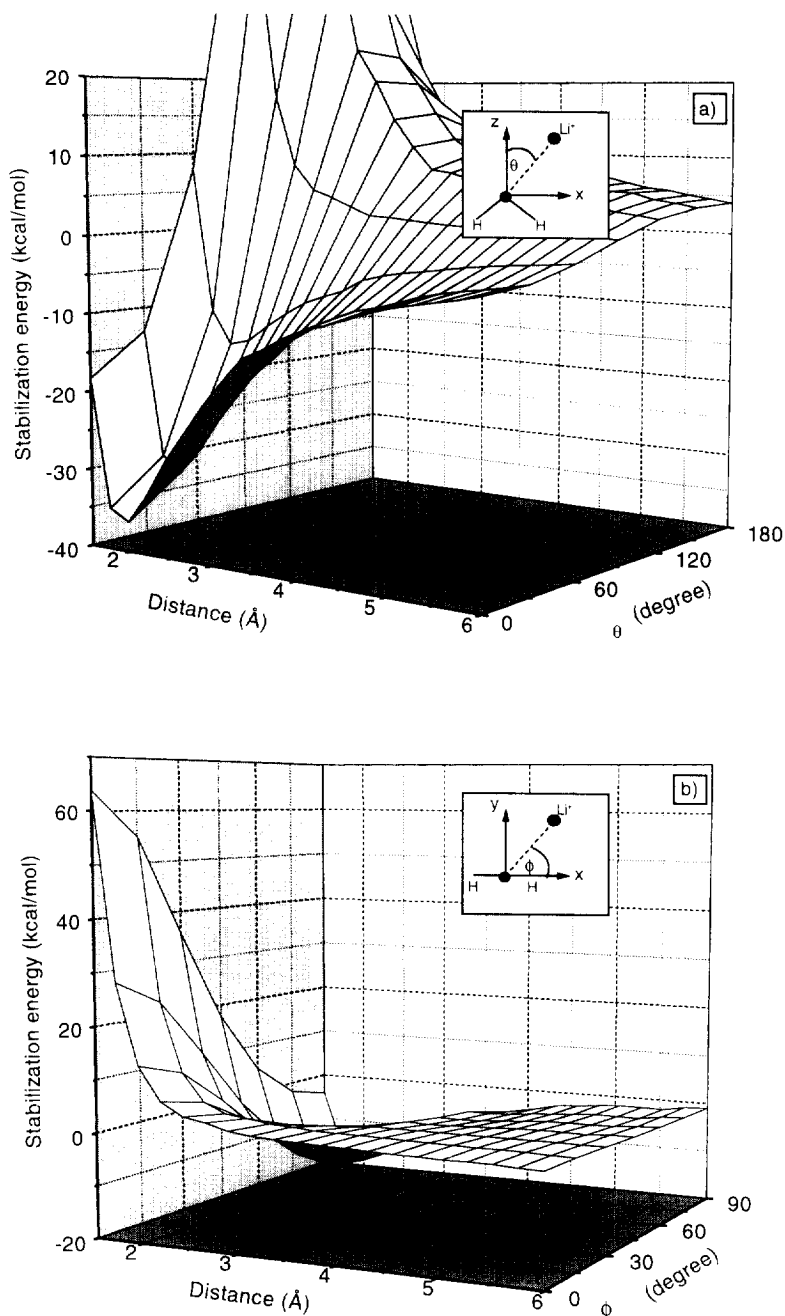


Fig. 1. Selected parts of the potential energy surface of the fitted function with respect to some movements of Li^+ around the water molecule. (a) ϕ is fixed at 0° and θ varied. (b) θ is fixed at 90° and ϕ varied.

average coordination number of 4.1. The form of the RDF shows that an exchange of water molecules between the first and second hydration shell is most

likely to occur. Fig. 3 shows the probability distribution of the coordination numbers, calculated up to the Li^+ -O distance of 2.8 Å. A sole coordination

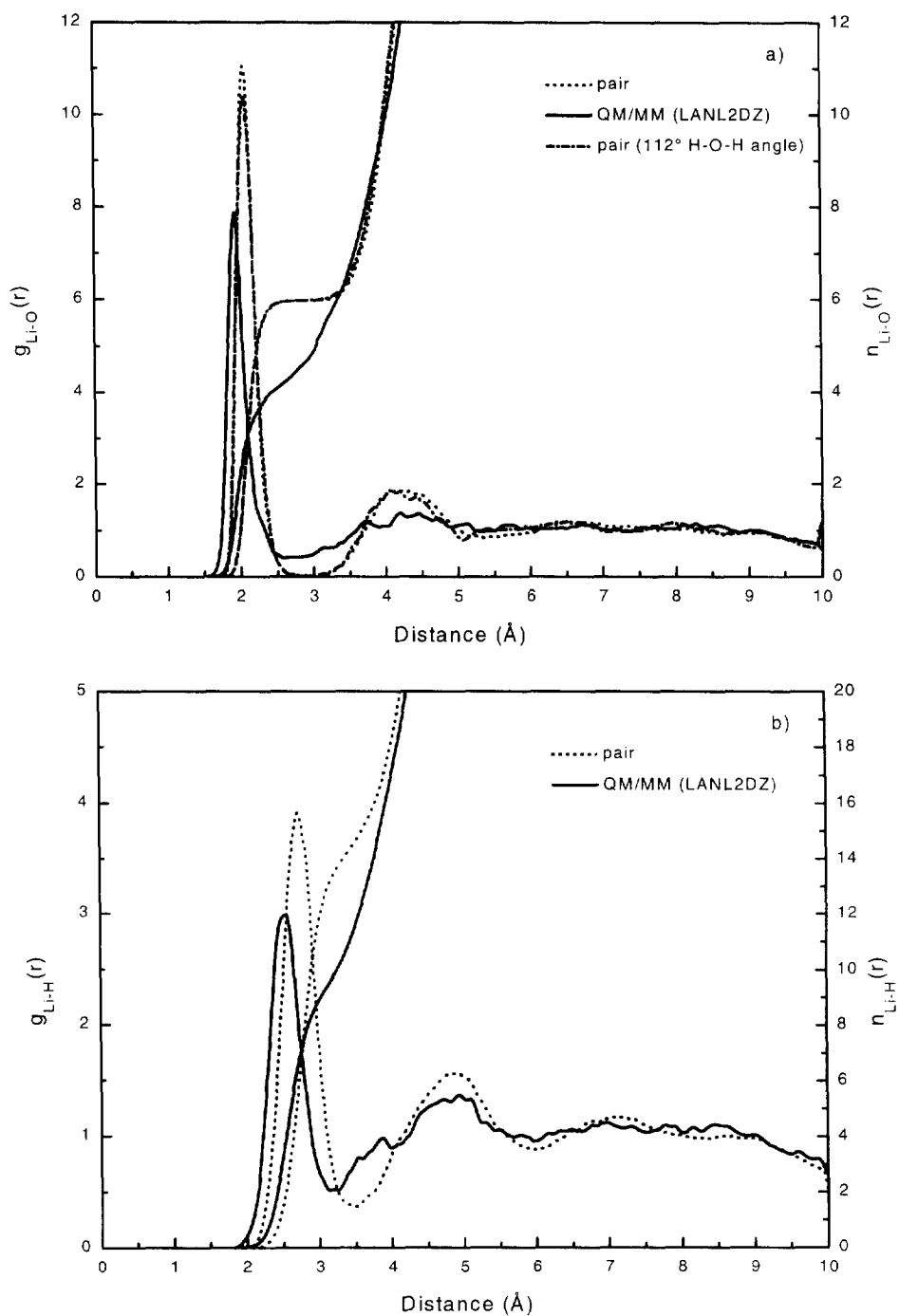


Fig. 2. (a) Li-O and (b) Li-H radial distribution functions and their corresponding integration numbers.

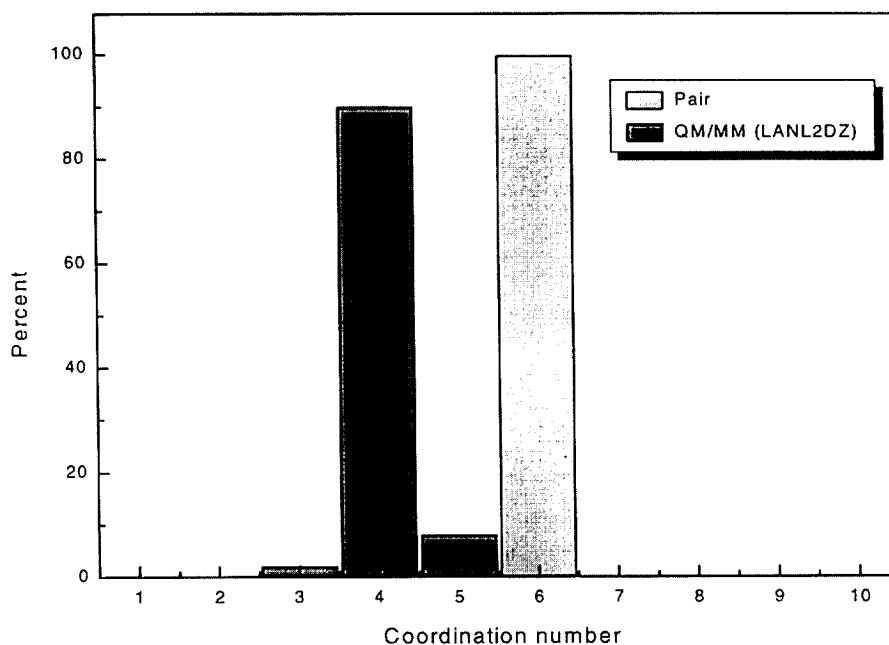


Fig. 3. Coordination number distributions.

number of 6 is found for the pair potential simulation, whereas 4 (in addition to 5 and 3 in decreasing amounts) is preferred for the combined QM/MM simulation. This simultaneous occurrence of these different coordination numbers is another strong indication for a continuous exchange process between the first and second hydration sphere. Table 3 gives a comparison of solvation parameters deduced from theoretical simulations and experimental investigations. The uncorrected pair potentials employed in this simulation yield a hydration number exceeding the experimental observations due to an overestimation of pair interaction energies, as to be expected from the *ab initio* calculations of $\text{Li}(\text{H}_2\text{O})_n^+$ complexes (see Table 1). An investigation of 3-body effects in $\text{Li}(\text{NH}_3)_2^+$ [32] has shown that at short Li–N1 and Li–N2 distances (N1 and N2 represent the first and second ammonia molecule, respectively), $\Delta E^{3\text{bd}}$ depends strongly on the N1–Li–N2 angle, and that most of these 3-body contributions are repulsive. Inclusion of 3-body terms reduced the coordination number from 6 to 4.4 [33], and a further reduction to a tetrahedral structure with four ammonia molecules in the first shell resulted from the QM/MM method [19], indicating that higher non-

additive terms still play a significant role. For the hydration shell of Li^+ , this seems to be true as well, as can be seen from the lowering of the coordination number from 6 to 4.1. Fig. 4 depicts the O–Li–O angular distributions up to the first minimum of the Li–O RDFs. The pair potential simulation shows an octahedral geometry by a well-pronounced peak around 90° and a small peak around 170° . In the QM/MM simulation, a re-arrangement to a tetrahedral structure is recognized from a broader peak between 105° – 110° , while the second peak vanishes. The coordination number of 3.9 reported by Degrève and Quintale [6] on the basis of a Monte Carlo simulation using the four-point transferable intermolecular potential (TIP4P) model for water is surprisingly similar to the result of our work, but this agreement is most probably an incidental one, and rather a consequence of technical inconsistencies, as the same TIP4P–water model in another work by Lee and Rasaiah [8] yielded a coordination number of 6. Most astonishingly a molecular dynamics simulation using the extended simple point charge (SPC/E) model for water in another paper of Lee and Rasaiah [7] resulted in the most similar hydration parameters, as well as the Monte Carlo simula-

Table 3
Comparison of hydration parameters for Li^+

Solute	Ion/water ratio or molarity (M)	r_{\max}	r_{\min}	n_{\min}	Method	Ref.
Li^+	1:199	2.06	2.72	6.0	CF2–water MD	this work
	1:199	1.94	2.60	4.1	QM/MM MD	this work
	1:125	1.98	–	5.3	MCY–water MD	[5]
	1:124	2.2	3.16	3.9	TIP4P–water MC	[6]
	1:215	2.20	3.10	6.0	TIP4P–water MD	[7]
	1:215	1.95	2.65	4.1	SPC/E–water MD	[8]
	1:525	2.0	2.8	4.5	TIP3P–water MD	[9]
	1:200	1.95	2.60	4.0	CI–water MC	[10]
LiCl	3.57 M	1.95	–	5.5	ND	[3]
	9.95 M	1.95	–	3.3	ND	[3]
	1.0 M	1.96	–	6.5	ND	[4]
	3.0 M	1.95	–	6.0	ND	[4]
	14.0 M	1.96	–	3.2	ND	[4]
	24.7 M	1.95	–	2.3	ND	[28]
	2 M	2.17	–	4	X-ray	[29]
LiBr	4 M	2.08	–	4	X-ray	[29]
	2.1 M	2.25	–	4(6)	X-ray	[30]
LiI	4.5 M	2.14	–	4(6)	X-ray	[30]
	5.6 M	2.16	–	4(6)	X-ray	[30]
LiI	2.2 M	2.13	–	6.1	ST2–water MD	[31]

r_{\max} , r_{\min} and n_{\min} are the distances of the first Li–O RDF maximum and minimum from Li^+ in Å, and the coordination number of the first hydration shell, respectively.

tions using CI-type for water–water interaction by Clementi and Barsotti [10]. The simple point charge (SPC) effective pair model considers the effects of polarizability by averaging them. The SPC/E model for water was adopted and reparametrized from the SPC model in which the effective pair potentials are improved by including a self-polarization energy. This correction emphasizes the need for a good (but simple) polarization model, but even with the proper correction, such effective pair potentials are a challenge to represent for polarizable systems [34]. Furthermore, especially for the first solvation shell of ions, some contributions are attractive, others repulsive and an average of them may hide problems leading to failures of some effective pair potentials.

Since the non-additive contributions increase at short interaction distances between ion and water, the most refined region for this work is therefore the first hydration shell of Li^+ . As the QM portion is the computationally most expensive part of our calculations the selection of the basis set is crucial. Ab initio geometry optimizations of $\text{Li}(\text{H}_2\text{O})_n^+$ with the LANL2DZ basis set yield rather reasonable structural properties with respect to calculations using

larger basis sets (e.g. DZV + P). Especially the difference in the ion–oxygen distance is found to be below 0.02 Å for $n = 4$ and 6. In the $\text{Li}(\text{H}_2\text{O})_n^+$ calculations, the ion–ligand interaction induces an increase of the H–O–H angle (see Table 1). This angle further increases in the QM/MM simulation with LANL2DZ basis set to $\sim 112^\circ$, whereas in the classical simulation a bond angle close to the experimental value of 104.5° is retained. This finding could suggest that the change in the coordination number could simply be a consequence of the different equilibrium angles of water. In order to analyze this point, another pair potential simulation was performed in which the angle for the intramolecular water potential was fixed at 112° . As shown in Fig. 2a, there is no change in the coordination number results with this larger H–O–H angle. It is obvious, therefore, that the observed change in the average coordination number must be due to the effects of many-body contributions in the hydration shell. The results could also be a guidance for studying the hydration structure of dilute solution system since the experiments (i.e. neutron diffraction) usually are subject to large errors at lower concentration [4].

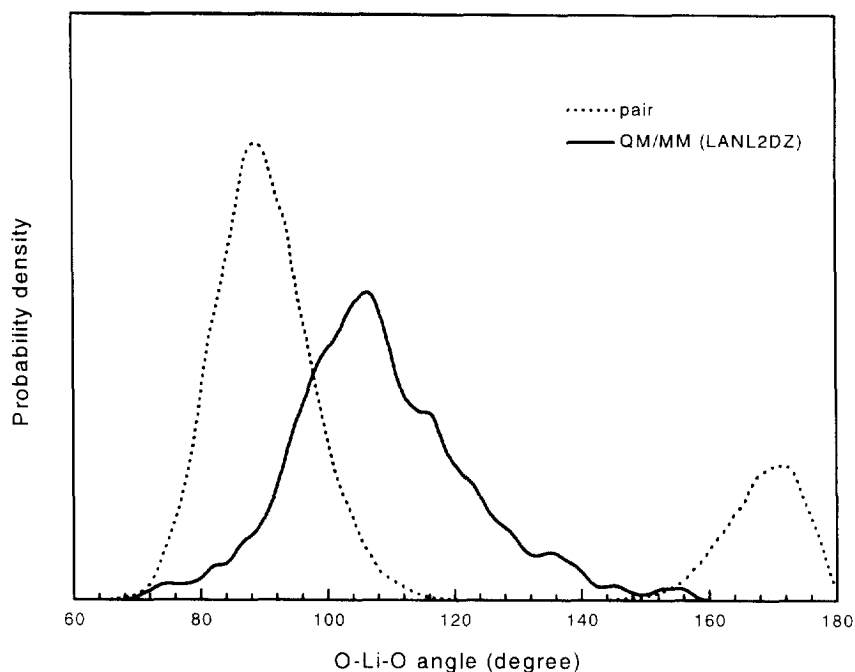


Fig. 4. O–Li–O angular distribution up to the first minimum of the Li–O RDFs.

The properties of the solvent itself are virtually the same in the classical pair potential and combined QM/MM simulation, as the sphere of the solvation shell calculated quantum mechanically comprises only about 5% of the overall volume of the system. The characteristic values of the solvent are in agreement with most classical pair potential simulations [20,35].

4. Conclusion

Combined QM/MM molecular dynamics simulation clearly predicts a tetrahedral first hydration sphere for Li^+ in water at low concentration, even though the employed *ab initio* method probably predicts a slightly too high Li^+ –water stabilization energy and therefore eventually slightly favours too high coordination numbers. Our QM/MM method, which simply calculates the forces within the first solvation shell around the ion directly from an *ab initio* calculation of the complete complex instead of using pair potentials relying on similar *ab initio*

methods, obviously demonstrates that simulations based on pairwise-additive approximations are not adequate and that non-additive terms can play a significant role, not only for the hydration of strongly interacting divalent ions, but also for the weaker hydration of monovalent ions such as Li^+ , where the ion–water interaction energy is $\leq 30 \text{ kcal mol}^{-1}$. Inclusion of higher terms, most probably up to the 4-body level appears necessary, therefore, for such systems. This seems to prove the need for more sophisticated simulation methods such as the QM/MM approach of this work, as the correction of analytical functions up to the 4-body level is definitely a more time-consuming and less elegant way.

Acknowledgements

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