

A Combined Quantum Chemical Statistical Mechanical Simulation of the Hydration of Li^+ , Na^+ , F^- , and Cl^-

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The hydration (or solvation) of the lithium, sodium, fluoride, and chloride ions are investigated using a combined quantum chemical statistical mechanical model. Radial distribution functions and the distribution of coordination numbers are reported and compared with other recent studies. An algorithm to investigate the geometry of the first solvation shell is proposed and applied to the four hydrated monatomic ions. The combined nature of the model enables an analysis of the coupling between the exchange repulsion and the induction energy. It is found that the coupling for the two cations is insignificant, while the two anions, especially the chloride ion, display a greater coupling between the exchange repulsion and the polarization. Induced dipoles and induction energies of the hydrated ions are also reported.

1. Introduction

When new models are developed for the investigation of aqueous solutions and other liquid systems it is common to theoretically study the solvation of monatomic ions. This is so, since systems of hydrated monatomic ions are simple compared with many other liquid systems, and are still of physical, chemical, and biological interest, and not only an artificial construction. These points are clearly evident when reading the review of Ohtaki and Radnai¹ on the topic of ions in solution. The invention of the well-known Metropolis-Monte Carlo method² marked the birth of computer simulations as a statistical-mechanical technique, and many models have been devised since then to study liquid systems.³ Along with the improvement of computers, the interest and the possibility of including quantum chemical methods in such models for the study of liquid-phase problems have increased. One of the most prominent types of such models are the QM/MM schemes, reviewed in ref 4. They are often used in the study of proteins where usually one region is treated with quantum chemical methods, while the remaining part—commonly called the spectator region—is treated with molecular mechanics (MM). There also exist variants of the QM/MM methods designed for simulation of solvated molecules; in these models the solute, together with solvent molecules closer to the solute than a prescribed distance, are treated quantum chemically, with the remaining solvent constituting the MM region.^{5–7} In a recent article, one such model was used in a molecular dynamics simulation to study dynamic properties of water molecules in the hydration shell of Na^+ and K^+ .⁸ Other models of a combined nature are mentioned in the literature, being either precursors to the QM/MM models of today or models with a different approach and/or different purpose than the QM/MM ones; for some examples and discussion (not exhaustive) see refs 9–14. The model applied in this work is a combined quantum chemical statistical mechanical one used previously for a number of small molecules.^{14–17} Generally speaking, the model divides the aqueous system into three interacting parts, one quantum chemical and one statistical mechanical part, both surrounded

by a dielectric continuum which constitutes the third part. At the end of the model section below, differences between this model and the typical QM/MM methods will be discussed.

The hydration under study in the present work is that of the four monatomic ions: the lithium, sodium, fluoride, and chloride ions. Radial distribution functions (RDF), distribution of coordination numbers (CN), and geometries of the first hydration shells are reported for each system. Further, a coupling term between the exchange repulsion and the induction energy is reported and explained. An assumption in most statistical mechanical models is that the exchange repulsive term and the polarization term can be added independently to the overall interaction energy; noteworthy exceptions are some so-called shell models or Drude oscillator models.^{18,19} This study provides a quantitative estimate of the error in that assumption for the solvation of the four ions in aqueous solutions. Due to the different polarizabilities and charges of the four ions, the estimates will afford an assessment of how the error depends on these two variables and therefore provide means to gauge the error for other aqueous systems. Our results are compared with recent studies.^{20–30}

In this article atomic units are used.³¹

2. Model and Computational Details

In this section the model and the computational details will be presented. The model is described in detail in ref 14, therefore only the principal features are recounted below.

As stated earlier, the aqueous system is divided into three parts. One part is described by the self-consistent field (SCF) model; this space is occupied by the ion in each simulation. The basis in which the Hamiltonian matrix is expressed cannot be too large since it would make the description of the quantum chemical part and the calculation of the interaction between the quantum chemical part and the statistical mechanical part (see later) too time-consuming. A further requirement of the basis, considering the polar environment of the quantum chemical part, is that it allows for a good description of polarization. To meet these demands, a molecular orbital (MO) basis is constructed in a manner resembling the averaging method by Widmark et

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TABLE 1: Basis Sets for the Ions^a

ions	contracted AO basis	number of MO
Li ⁺	10s4p3d.4s3p1d.	5
Na ⁺	13s8p3d.4s3p1d.	15
F [−]	10s6p3d.4s3p1d.	15
Cl [−]	13s10p4d.7s5p3d.	19

^a Ref 34.

al. for the design of atomic natural orbitals (ANO)³² with the quantum chemistry package Molcas 5.³³ The construction starts with equipping the ion with a contracted ANO-basis, see Table 1.³⁴ Eight different density matrices are subsequently calculated for each ion, all in a different electrostatic environment: one with no electric field applied, six with a field (0.002 au) applied along each axis in positive and negative direction, and finally one with the ion placed in a so-called well, restricting the extension of the electrons. An average density matrix is computed from these eight density matrices. The molecular orbitals with the largest occupation number that are obtained when diagonalizing the average density matrix are taken as the basis functions used to describe the quantum system, see Table 1.

The second part contains all the discrete water molecules (89 in each simulation). To describe interactions between the water molecules, an intermolecular water–water potential constructed by an early version of NEMO is used.³⁵ It includes electrostatic, exchange, and dispersion interactions, and also accounts for many-body effects, with the so-called point dipole induction model. The potential surface is constructed fitting parameters in expressions consistent with theory to surfaces obtained from SCF calculations on different structures of the water dimer. For details and parameter values see ref 35.

Finally, a dielectric continuum encompasses the two previous parts. In line with the work of Friedman,³⁶ the dielectric surrounding is modeled with the image charge approximation. The approximation involves representing the reaction field to a set of molecules inside a cavity as a set of multipoles located in the continuum; the image of a point charge inside the cavity is another point charge in the continuum, while the image of a dipole is a dipole and a point charge. In the model, only images originating from charges and dipoles are included. This way the electrostatic effects that water molecules in the complement to the two previous parts have, are taken into account by the model.

To complete the description of the aqueous system, the model must also account for interactions between the three parts. The most intricate type of interaction is that between the quantum chemically described ion and the surrounding discrete water molecules. To be consistent with the SCF approach, electrostatic and exchange interactions are to influence the Hamiltonian matrix of the ion. To include the first type of interaction, the charge density of the ion (expressed in the ANO-basis) is multipole-expanded (ME), in other words described as a set of multipoles.³⁷ These multipoles then interact with the multipoles on the water molecules. The electrostatic interaction is added to the Hamiltonian matrix expressed in the MO-basis and the electrostatic properties of the ion are recalculated and allowed to polarize the solvent. By iterating this procedure, the electrostatic interaction, including polarization, between solvent and ion is accounted for.

Turning to the exchange repulsion between the ion and water, its influence on the matrix elements h_{ij} is contained in a term r_{ij} added to each element, $h_{ij}' = h_{ij}(1 + r_{ij})$. It is known that the exchange repulsion between two species is approximately

proportional to the orbital overlap, S , raised to the power of two.^{38,39} Therefore, each water molecule is imbued with five molecular orbitals, i.e., only occupied orbitals, to enable the computation of this quantity. These orbitals are obtained with the same averaging scheme used to construct the orbitals of the ions. During the simulation these orbitals are not optimized. Given these considerations and prerequisites an expression for r_{ij} is formulated:

$$r_{ij} = \sum_{\alpha \in \Omega} \sum_k r_{ij}^{\alpha,k} \quad (1)$$

$$r_{ij}^{\alpha,k} = d \cdot \zeta(k) \sum_n \sum_m (S_{ik} s_{jk}(m, n) + S_{jk} s_{ik}(m, n)) \quad (2)$$

where S_{ij} is the orbital overlap between quantum orbital i and orbital k on water molecule α . The contribution that the overlap between basis functions centered on atoms of type m in the quantum chemical part and the atoms of type n in the classical part makes to this orbital overlap is denoted $s_{ik}(m, n)$. The factor $\zeta(k)$ is the orbital energy of water orbital k . It gives greater weight to overlap with orbitals with low orbital energies. Its justification is that the effect on the electronic structure of the ion, i.e., on the Hamiltonian matrix elements, that the exchange repulsion has, depends on which electrons are forced to adjust to avoid violation of the Pauli principle. For example, a strongly bound electron in water will upon overlap with an electron of the ion engender a greater change in the electronic structure of the ion than a weakly bound electron of the water. Since exchange repulsion declines rapidly with increasing separation, water molecules farther away than 10 au from the ion are not included in the set Ω of solvent molecules which in the model contribute to the perturbation r_{ij} . Finally, d is a parameter to be fitted in a manner described below. In describing the exchange repulsion at small separations, however, the term proportional to S^2 is not sufficient and alone fails to reproduce the very steep increase in potential energy at such distances. The addition of

$$\beta_4 \sum_i S_i^4 + \beta_6 \sum_i S_i^6 + \dots$$

to the total interaction energy is necessary in order to achieve this reproduction. S_i is the orbital overlap between MO i and the orbitals of the water molecules in the set Ω . Higher-order terms can also be included, and for the chloride ion it was found necessary to do so. It should be noted that the Hamiltonian matrix elements are not perturbed by any higher-order term.

The SCF method does not include second-order effects such as dispersion interaction. There is thus no consistent way to include this interaction in the Hamiltonian matrix. Still, dispersion interaction contributes significantly to the overall interaction energy, its inclusion is thus expedient to the aims of the model. This is achieved in what is commonly called a phenomenological manner: to the term containing the electrostatic and exchange interaction between the quantum chemical part and the classical part, a term accounting for the dispersion is added. Its functional form is $1/r^6$ where r is the distance between a certain atom of the solvent molecule (i.e., hydrogen or oxygen in our particular case) and the ion. Two parameters are needed for each ion: one for the dispersive interaction between ion and hydrogen (denoted $D_{k,H}$ in Table 2), and one for ion-oxygen (denoted $D_{k,O}$ in the same Table). The functional form is however false at short distances since it is derived under the assumption that the species are not overlapping—an assumption that leads to too great an attraction at small separations. A convenient correction to this

TABLE 2: Value of Model Parameters As Described in the Section Model and Computational Details

parameter	Li ⁺	Na ⁺	F ⁻	Cl ⁻
$D_{k,O}$	0.12988	10.6581	14.0803	127.055
$D_{k,H}$	0.02887	2.3368	3.0173	28.1753
d	-0.1850	-0.04640	-0.01395	-0.00995
β_4	3.0	0	0	0
β_6	0	250.0	62.0	25.0
β_{10}	0	0	0	1000
γ				0.5

error has been developed by Tang and Toennies in the form of a damping function.⁴⁰ The product of this function $f_6(r)$,

$$f_6(r) = 1 - \left(\sum_{k=0}^6 \frac{(br)^k}{k!} \right) e^{-br} \quad (3)$$

and the expression proportional to $1/r^6$ is taken as the dispersion interaction at all separations; as r tends to infinity, the damping approaches unity and the nondamped dispersion expression is obtained. The parameter b in the damping function is the so-called Born–Mayer parameter. In the original text by Tang and Toennies, b is fitted to SCF potentials. Since the Born–Mayer parameter is related to the extension of the electrons of the molecule or atom in question, a scheme could be devised that, given certain quantities of the species, calculates a reasonable parameter value; Brdarski and Karlström suggest one such scheme that uses localized second moments and partial charges.⁴¹ With the Born–Mayer parameters (two for each ion) computed with this scheme, the dispersion in the present model is damped with the Tang–Toennies damping function.

Obtained under the same assumption, there are consequently errors in the multipole expansion^{39,42} causing the electric field to become too large at small separations, thus exaggerating the polarization of the ion. The error is tractable for the three least polarizable ions, while for the very polarizable chloride ion there is reason to seek a remedy. Hence, in the model the electric field on the chloride ion from the nearest water molecules is damped according to

$$E' = E(1 - e^{-\gamma r})^3 \quad (4)$$

where r is the distance from the ion to the site on the water molecule used as a center for either a partial charge or a dipole; γ is a parameter.

To obtain numerical values of the parameters of the model, an intersection of the pure pair-potential surface for the ion–water system is computed. To begin with, the geometry optimum on SCF-level of the ion–water system is obtained, under the constraint that the geometry of the water molecule is frozen in the experimentally found geometry of liquid water, i.e., bond length 1.8084 au and bond angle 104.51°. In steps of 0.2 to 0.3 au, the water molecule is translated closer to, or farther from, the ion relative to the optimum. When translating the water molecule relative to the ion, each atom in the water molecule is moved parallel with the vector joining the ion and the closest water atom. In each point the SCF and the MP2 energies are computed, with corrections for basis-set superposition error (BSSE) with the counterpoise method.⁴³ An intersection is thereby obtained as a function of the distance between the ion and the closest water atom. The expression for the dispersion interaction of the model derives from perturbation theory, hence the dispersion parameters can be fitted to the second-order energy corrections for intermolecular distances somewhat larger than the equilibrium distance where the overlap between the

two species is small (and thus the assumptions of the perturbation theory are valid). A complication is, however, due to the significant difference in the computed dipole moment of the water molecule using either SCF or MP2 (observed for other molecules as well^{44,45}); since the system is ionic this will have rather long-ranged effects, contaminating the second-order energy corrections with a term not related to the London forces. By computing with both SCF and MP2 the interaction energy at two very distant points, where it is reasonable to assume that only the charge–dipole interaction is of importance, the difference in charge–dipole interaction is evaluated and the contamination is sufficiently eliminated.

With the dispersion parameters deduced and a set of trial parameters for the exchange repulsion, the energy in each point where an MP2 energy has been computed is calculated with the model. The exchange repulsion parameters are then modified until the intersection obtained with MP2 is reproduced well. For the chloride ion the parameter in the exponential expression responsible for the damping of the electric field is also adjusted along with the exchange repulsion parameters; the effort is however to keep the damping small. All values of the parameters are presented in Table 2.

The model bears a resemblance to the popular QM/MM methods; there are however a few significant points in which it departs from the typical QM/MM scheme. To conclude this section, we highlight these differences. The most critical selection in a QM/MM calculation is the size of the QM-region, both in terms of accuracy and consistency as well as the computational requirement; typically, the QM-region includes the solute and the solvent molecules in the first solvation-shell,^{6,8} although Loeffler and Rode use a larger QM subset in their study of Li⁺ since they found that it was necessary in order to avoid artifacts.²⁶ It means that there will be a discontinuity in the modeled system and thus two kinds of solute–solvent interactions. Also in the present model there are two kinds of solute–solvent interactions (discrete water and continuum water interacting with the quantum chemical center), but the radius of the cavity can be much larger than the radius of the QM-region in QM/MM without making the computation infeasible. In other words, the solute–solvent interaction is described more consistently in the present model than in QM/MM. On the other hand, the treatment within the QM-region in QM/MM is more accurate, if it is plausible to assume that the less accurately described MM-region interacts reasonably correctly with the QM-region, especially with the solute in the center of the QM-region. If there are reasons to doubt this assumption, the configurations obtained in the simulation might be a poor representation of the simulated physical system. It is especially in the treatment of the exchange repulsion in the present model that makes the discontinuity in the system less drastic. In the typical QM/MM methods the van der Waals interaction (dispersion and exchange repulsion) follows the Lennard-Jones potential or possibly some other pair-potential.^{5,46} The use of the orbital overlap between the quantum chemically described part and the water molecules, as in the present model, instead of the separation of the nuclei as the variable in the function for the exchange repulsion, makes the treatment more quantum chemical in its character. Clearly, each solvent molecule in the present model has a combined quantum mechanical classical mechanical nature, being equipped with both orbitals and point charges and polarizabilities.

Given that a sufficiently large QM-region is used, QM/MM is expected to be more accurate than the present model. But since a larger QM-region implies a higher computational effort—

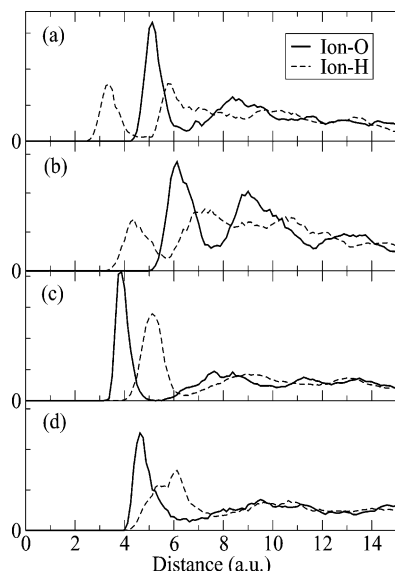


Figure 1. Radial distribution functions for (a) F^- , (b) Cl^- , (c) Li^+ , and (d) Na^+ .

TABLE 3: Table of the Numerical Simulation Result. $\langle X \rangle$ Is the Mean Value of X and $\text{STD}(X)$ Denotes the Standard Deviation of X . $r_{\text{max},X}$ and $r_{\text{min},X}$ Are the Location (in a.u.) of the Maximum and the Minimum of the Ion- X RDF. μ_{ind} Is the Induced Dipole and U_{ind} Is the Induction Energy

	Li^+	Na^+	F^-	Cl^-
$\langle \text{CN} \rangle$	4.00	5.85	4.68	6.25
$\text{STD}(\text{CN})$	0.04	0.76	0.47	0.74
$r_{\text{max},\text{H}}$	5.13	6.1	3.13	4.38
$r_{\text{max},\text{O}}$	3.88	4.63	5.00	6.13
$r_{\text{min},\text{H}}$	6.38	7.6	4.88	5.75
$r_{\text{min},\text{O}}$	5.25	6.63	6.50	7.5
$\langle E_{\text{coup.}} \rangle \times 10^3$	-0.019	-0.041	-0.079	0.73
$\text{STD}(E_{\text{coup.}}) \times 10^3$	0.0024	0.018	0.14	0.27
$\langle \mu_{\text{ind}} \rangle$	0.0026	0.0031	0.075	0.35
$\text{STD}(\mu_{\text{ind}})$	0.0009	0.0011	0.025	0.14
$\langle U_{\text{ind}} \rangle$	-2.7×10^{-5}	-2.3×10^{-5}	-0.0020	-0.0047

how much will depend on which quantum chemical model that is used—it will, at least for larger molecules, be difficult to meet this prerequisite. Various simplifications of the QM/MM treatment have been suggested with the aim of making it more efficient, with the prospect that larger QM-regions can be used and thus to some extent satisfy the prerequisite.^{46–48} The present model is another way to a less computationally costly model that still utilizes the advantages of combined quantum chemical statistical mechanical description.

3. Results and Discussion

A Monte Carlo simulation of 100 000 steps where all water molecules are moved in each step of an equilibrated system is performed, and a set of 1200 configurations are stored and used as a representative selection for the statistical analysis that follows below. One such analysis is the inference of two radial distribution functions (RDF)⁴⁹ for each ion: the location of the hydrogen atoms and the oxygen atoms of the water molecules relative to the ion. The RDFs for all the ions are presented in Figure 1 and in Table 3 are the first maximum and minimum of the RDFs reported. The value of the RDF in the first minimum is close to zero for the fluoride or lithium ion, while the RDF for neither the chloride or the sodium ion display such behavior. Beyond the first solvation shell the water molecules demonstrate a slight structure, but it is too diffuse to enable any reasonable assignment of the extension of a possible second

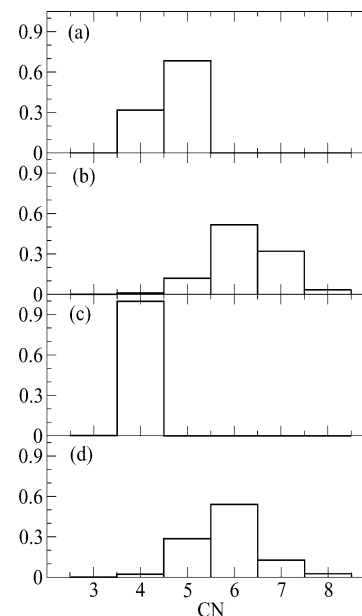


Figure 2. Distribution of coordination numbers for (a) F^- , (b) Cl^- , (c) Li^+ , and (d) Na^+ .

solvation shell. The RDF of the chloride ion, with a pronounced second peak in the ion-oxygen radial distribution, departs from this pattern. The high polarizability of the chloride ion could explain why this particular ion manifests more long-ranged solvation structure; a nonphysical explanation could be that structure at the dielectric boundary influences the structure at intermediate distances from the ion, which in interplay with the greater size of the chloride ion, constructively interferes with the slight structure there already is at such distances.

The number of solvent molecules adjacent to a solvated species is called its coordination number (CN). The mean CN is possible to obtain by integrating the first peak of the (normalized) RDF and multiplying that quantity with a suitable constant. In a simulation it is also possible for each configuration to count the number of solvent molecules within the boundary of the first shell, as deduced from the RDF. In this way the distribution of the CNs is available; the results are shown in Figure 2. The lithium ion and the fluoride ion have the least distributed CN. This is in agreement with the fact that the minimum of their RDFs is almost zero, i.e., few water molecules pass either in or out of the first solvation shell. Ranging a wider spectrum of CN, the first solvation shell of the sodium and chloride ion appears on the other hand to be less distinct and more open to water molecules entering and leaving; this is consistent with their respective RDFs.

In the review of the study of ions in solution by Ohtaki and Radnai¹ the results of several theoretical studies are collected. The RDFs and the mean CN obtained in the present work do not differ spectacularly from the collected results, but lie within the rather broad intervals of results predating the review. More recent results also span rather wide intervals, and the present result is not stretching the bounds of these intervals either. In a more specific comparison with other recent studies, a number of remarks are due. Most often the CN for the lithium ion is found to be four or slightly higher,^{21,25–28,30} but there are studies that depart from this;^{20,22} the present result belongs to the former group with an inferred CN equal to four with a very small standard deviation, see Table 3. It is more difficult to compare different RDFs. What can be seen in all studies however is that the $\text{Li}^+ - \text{O}$ RDF usually reaches very small values, indicating a well-defined first solvation-shell. For the sodium ion, such

nice agreement between the different RDFs is not found. Some studies obtain RDFs with qualitative features similar to the lithium ion,^{22,27} while others report RDFs that look similar to ours, i.e., having a first minimum significantly elevated above zero.^{20,24,30} Also with respect to CN and distribution of CN, disagreements are found. The properties of the hydration of the sodium ion thus appear to be less clear-cut vis-à-vis the lithium ion, consequently making the obtained data more sensitive to the choice of the model. Comparing the results for the anions, it is found that all studies conclude like the present one that, first the RDF for the F^- –H separation has a well-defined minimum with a value close to zero,^{20,22,27} and second that the RDF for the Cl^- –H distance is visibly far from zero in its first minimum.^{20,22,27,28} There is less agreement between the obtained CN, however. With a mean CN of 4.68 the present study is positioned in the lower end of inferred CN; commonly this value is around six.^{20,22,27} Since all studies conclude that the first solvation-shell of the fluoride ion is well-defined, the CN is a well-defined quantity, thus the difference cannot be rationalized so easily. This seems to be the result in the present study that departs the most from that of other recent studies. With a less well-defined first solvation-shell, the difference in computed CN for the chloride ion (from 5.73²² to 7.2²⁸) is not as remarkable.

The RDFs reveal structural features of how the adjacent water molecules solvate the ions. For a start it is concluded that the oxygen atom of the closest water molecules is facing the cations, while it is one of the two hydrogen atoms that points toward the anions. This result is not anomalous, considering that the charge distribution of the water molecule is such that the oxygen atom carries more negative charge than the hydrogen atoms. Looking at where the ion–hydrogen RDF starts having nonzero values relative to the ion–oxygen RDF, it is seen that for the sodium ion it happens almost at the same distance, while for the lithium ion there is a visible separation. So, in contrast to the lithium ion, there exist configurations for the solvated sodium ion where the hydrogen atoms are almost as close to the ion as the oxygen atom. Thus, assuming a fixed sodium ion–oxygen distance the water molecules solvating the sodium ion seem less restricted in their other degrees of freedom than the corresponding water molecules in the system containing the lithium ion.

To investigate the geometry of the first solvation shell as a whole and not the preferred alignment of individual water molecules relative to the ion, the following algorithm is used. In a given configuration for a cation, the two oxygen atoms in the first solvation shell that are farthest apart define the z -axis. Of the remaining first-shell oxygen atoms, one is chosen randomly and defined to be a point on the x -axis, therefore also defining the xy -plane. In this coordinate system the polar angles of the CN-3 remaining first-shell oxygen atoms are computed. For an anion the closest hydrogens are used instead. Since polarizable ions inside the “cage” of the first solvation-shell often assume a position closer to one boundary than the other,⁵⁰ it is advantageous to exclude the ion from the construction of the coordinate system, because its inclusion would blur the sought information. Further, the information produced by this algorithm will be of a small amount yet specific.

In Figure 3 the result from this investigation for the lithium ion is graphically presented. Figure 3(a) is a histogram of the set of angles in the xy -plane, called θ , and ranging the interval zero to 360 degrees. Figure 3(b) is a scatter plot between θ and $\cos \xi$ where ξ is the angle with the xy -plane, sometimes called the azimuthal angle. Since the CN is four for as good as every

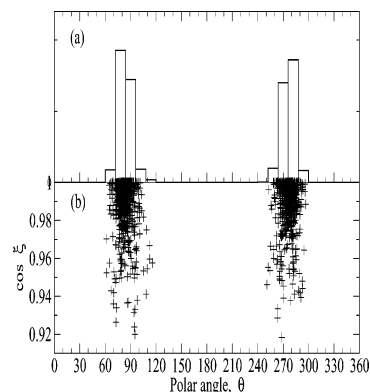


Figure 3. For the lithium ion, (a) distribution of polar angles for configurations with CN = 4 and (b) scatterplot of polar angles and $\cos \xi$ for the same configurations.

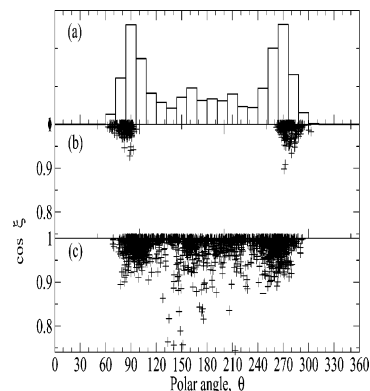


Figure 4. For the fluoride ion, (a) distribution of polar angles for all sampled configurations, (b) scatterplot of polar angles and $\cos \xi$ for configurations with CN = 4, and (c) scatterplot as in (b) but for configurations with CN = 5.

configuration of the lithium ion, the ideal structure of the first solvation-shell would be a tetrahedron. By definition, there is a water molecule in the point ($\theta = 0^\circ$, $\cos \xi = 1$), therefore the cluster of points in Figure 3(b) near ($\theta = 70.5^\circ$, $\cos \xi = 1$) — where an ideal tetrahedron would have a peak — does not conflict with the proposition that the water molecules of the first solvation-shell form a slightly perturbed tetrahedron around the lithium ion. (Observe that the symmetry in Figure 3 and all corresponding figures for the other ions follows from how the coordinate system is constructed.) Both Lyubartsev et al.²⁵ and Loeffler and Rode²⁶ also find this geometry of the first solvation-shell, although the lack of a good quantitative measure of how perturbed the structure is in each study prevents investigation of how similar the structures really are. In Figure 4 the parallel results of the first shell of the fluoride ion are presented. In Figure 4(a) is a histogram of θ for all stored configurations. Since the CN of the fluoride ion is significantly both four and five, two scatter plots are presented: in Figure 4(b) only configurations with CN = 4 are displayed, in Figure 4(c) the remaining configurations with CN = 5 are considered. Figure 4(b) looks very much like Figure 3(b) of the lithium ion and a similar conclusion is drawn. With five adjacent water molecules two structures appear to be ideal: the trigonal bipyramid and a pyramid with a rectangular base. Figure 4(c) suggests that both these structures exist in perturbed form in the set of configurations with CN = 5. The denser parts around ninety and 180 degrees can be due to the later structure, while the points close to 120 degrees is consistent with the existence of the former. Several points are located outside and between these two regions, which suggests that no high energetic barrier exists

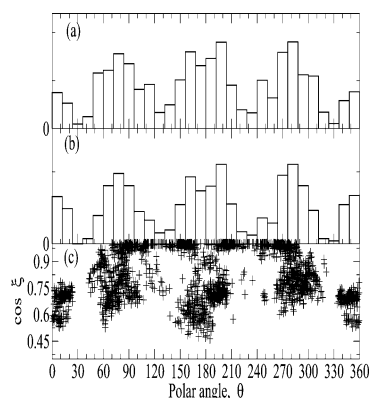


Figure 5. For the sodium ion, (a) distribution of polar angles for all sampled configurations, (b) distribution of polar angles for configurations with CN = 6, and (c) scatterplot of polar angles and $\cos \xi$ for configurations with CN = 6.

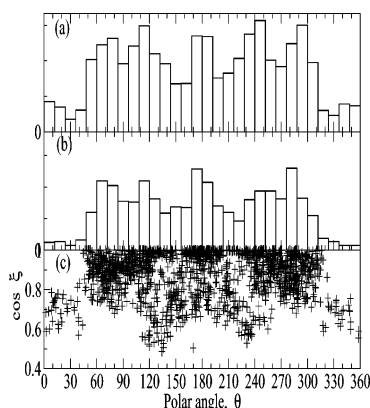


Figure 6. For the chloride ion, (a) distribution of polar angles for all sampled configurations, (b) distribution of polar angles for configurations with CN = 6, and (c) scatterplot of polar angles and $\cos \xi$ for configurations with CN = 6.

between the two structures, thus enabling frequent shifts between them and occupations of intermediate states. Figure 5(a) is diffuse and does not suggest which structure is prevalent for the hydrated sodium ion. This is no surprise, considering the wide range of CN. In Figures 5(b) and (c), only configurations with CN = 6 are considered. An octahedron is the ideal structure in this case. There are clusters of points near $\theta = 90^\circ$ and $\theta = 180^\circ$ where an octahedron would have peaks; however, these clusters are very dispersed, both in terms of θ and most of all in terms of $\cos \xi$. Further the points near $(\theta = 0, \cos \xi = 0.7)$ are in obvious conflict with the existence of an octahedral structure. These points do, however, suggest that two water molecules are rather close to one another (since there, by definition, is a water molecule located at $(\theta = 0, \cos \xi = 1)$). Finally, the results of the chloride ion resemble those of the sodium ion, as seen in Figure 6. When only configurations with CN = 6 are analyzed (Figures 6(b) and (c)) instead of all sampled configurations with their multitude of CNs (Figure 6(a)), the hypothesis of the prevalence of an octahedral structure is firmly rejected.

These results—the RDFs, the distributions of CN, and the investigations of the first solvation-shell structure—support the following conclusions. (1) The lithium ion is strongly hydrated, i.e., interacts strongly with the surrounding water. (2) The fluoride ion is also strongly hydrated, which due to its size is less obvious since the general trend is that larger ions form weaker bonds with water molecules. (3) Both the sodium ion and the chloride ion impose a less distinct structure on the nearby

water molecules than the two other ions; it is interesting that despite its relatively small size, the sodium ion does not break the water–water bonds in favor of the sodium–water ones very much, which probably is due to the donor/acceptor properties of water. Although both the sodium and the chloride ion share the feature of not imposing a distinct structure on the adjacent water molecules, there is obviously a difference in the structure of the coordinated waters, as is readily seen when contrasting Figures 5(c) and 6(c). The coordinated water molecules of the sodium ion appear to be more ordered in some kind of structure (although not an octahedron), relative to the waters coordinated to the chloride ion. One conjecture is that the water–water interaction to a large part determines the structure of the six-coordinated water molecules, while the very polarizable chloride ion breaks the water–water structure, but favors very asymmetric or random structures that engender large electric fields (relatively speaking) on the ion. This would mean that the chloride ion, like the lithium and the fluoride ions, breaks the water–water structure, but does not substitute that structure for another specific one.

The model is, as described earlier, a combined quantum chemical statistical mechanical one. It implies that the electrostatic energy, the induction energy included, and the exchange repulsion are not independently added to the overall energy. Instead this energy contribution is obtained upon diagonalization of the Hamiltonian matrix. It is however possible in the analysis to “switch off” the exchange repulsion (set all exchange repulsion parameters to zero) and the polarization of the ion (only include the lowest occupied orbitals in the MO-basis). This way the coupling between the exchange repulsion and the polarization can be investigated. For each stored configuration four single-point energies are computed: E_1 , which is the energy when both exchange repulsion and polarization are “switched on”; E_2 and E_3 are energies when one of the two contributions is active while the other is not; and finally E_4 which is the energy when neither exchange repulsion or polarization adds to the overall energy. If the two energy contributions are independent the equation

$$E_1 = E_4 + (E_2 - E_4) + (E_3 - E_4) \quad (5)$$

would hold. If the two contributions couple however, a term $E_{\text{coup.}}$ would be necessary to add to the right-hand side of the equation. In Figure 7 the distributions of this coupling term are presented. The two least polarizable ions—lithium and sodium—have very small negative coupling terms. (A negative coupling means that the coupling between the induction and the exchange repulsion stabilizes the system.) It is therefore a tenable assumption that the exchange repulsion and the induction energy are independent terms in the overall energy expression for these two ions. The coupling term for the fluoride ion ranges a wider energy interval, also including positive terms. The most significant coupling is found for the chloride ion, and it is, without exception, positive. The origin of the coupling term can be understood as the change in overlap between the ion and the water molecules when the ion is allowed to polarize. If the electric field on the ion is such that the charge distribution is redirected away from the surrounding water molecules, possibly through an empty space in the “cage” of the coordinated water, the overlap S decreases and with that the exchange repulsion. Since a more polarizable molecule will when polarized alter its charge distribution to a greater extent, the coupling will in absolute numbers be greater. This is also what is found. With a diffuse charge distribution the chloride ion can probably not be polarized in a way that decreases the overlap with the

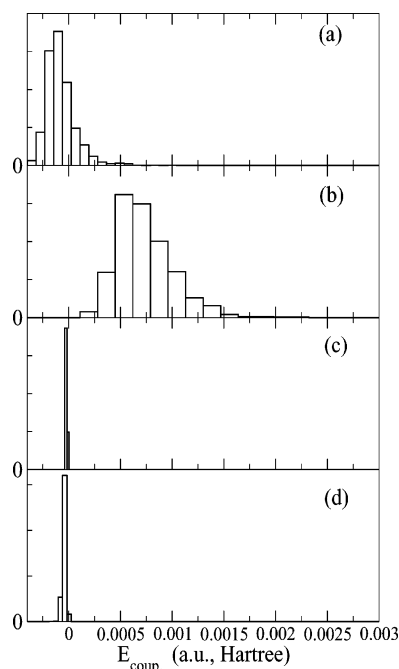


Figure 7. Energy coupling term between exchange repulsion and induction energy for (a) F^- , (b) Cl^- , (c) Li^+ , and (d) Na^+ .

water molecules, thus explaining the exclusive positive coupling in Figure 7(b).

It should be noted that in the simulation the occupied orbitals of the water molecules are not relaxed. The polarization of the water molecules is only represented as a set of ideal induced dipoles; in other words, the change in the finite extension of the charge distribution of the solvent upon polarization is not included in the treatment. For the two cations, we argue that the inclusion of the relaxation of the solvent would give a positive contribution to the coupling. The argument is that the diffuse (relative to the cations) charge distribution on the oxygen atom facing either the lithium or the sodium ion will be polarized in such a way that it comes closer to the charge distribution of the respective cation. The overlap between solvent and cation will thus increase and therefore also the exchange repulsion. Naturally, the charge distribution of the cation will respond and be redistributed and consequently lower the exchange repulsion as well as increase the polarization, but given that the two cations are not particularly polarizable, the net effect will probably be positive. The relative difference between the coupling for the anions with or without relaxation of the water orbitals will very likely be small. Since both anions have very diffuse charge distributions, their relaxation will probably be more significant to the coupling than that of the solvent. Whether the ability to relax the solvent orbitals has any significant effect on how the waters orient themselves around the ion, is difficult to reason about. Since only energy differences matter in the sampling, it is necessary not only to know that the computed single-point energies differ, but also whether the size of the change is different in different points in the equilibrated configuration subspace. The existence of such points is almost certain, especially in configurations where the ion is very close to a water molecule, but their significance is on the other hand uncertain. It is probable, though, that by introducing the ability to redistribute the charge distribution of only the ion, the major alteration of the solvation structure in the vicinity of the ion compared to a model without a connection between polarization and exchange repulsion has been included; the effect the relaxation of the orbitals of the water molecule will have is

therefore probably small. These propositions are only conjectures whose correctness remains to be properly tested.

In the literature of quantum chemistry the concept of *exchange polarization* exists.^{51,52} It is the correction to the second-order terms when exchange repulsion is considered. The coupling term E_{coup} is concerned with the change in polarization of the ion when exchange repulsion is considered (or vice versa) and therefore is related to the concept of exchange polarization. E_{coup} does however not take into account any intramolecular changes and is not obtained treating the ion and the water at the same level of theory; therefore, E_{coup} should *not* be considered as a numerical estimate of the exchange polarization.

In Table 3 are induced dipole moments and induction energies (computed in the same way as in the calculation of the energy coupling) for the four ions presented. Neither of the two cations has large induced dipole moments or induction energies. Both the fluoride and the chloride ions have much larger values. Since the two latter ions have larger polarizability than the two former, this result is expected. To conclude, it would not constitute an extreme loss of accuracy to neglect the polarization of the two cations in a model for their hydration. (The polarization of the water molecules plays, on the other hand, an important role for the hydration of these two ions.⁵³) For the anions, the neglect of polarization would be a more serious deficiency for a theoretical model.

4. Summary

We have performed a Monte Carlo simulation of the hydration of the lithium, sodium, fluoride, and chloride ions, using a combined quantum chemical statistical mechanical model. The ion is described quantum chemically with the self-consistent field (SCF) model, while the surrounding water molecules are described classically, with many-body effects included. The radial distribution functions, distribution of coordination number, and geometry of first solvation-shell are inferred and compared with the corresponding results of other recent studies. No extreme differences are found, although a number of noteworthy similarities and distinctions are revealed when contrasting the different studies: All find the interaction between the lithium ion and the adjacent water molecules to be strong, while no consensus exists regarding the nature of the solvation of the sodium ion. All our results suggest, however, that the sodium ion forms comparatively weak bonds with the nearby water molecules. The conclusions of the present study regarding the two anions only show obvious difference relative to other studies with respect to the inferred coordination number of the fluoride ion. Otherwise there is agreement that the fluoride ion, in contrast to the chloride ion, structure distinctly the coordinated water molecules. The investigation of the first solvation-shell geometry shows that, although they share the property of not having a first solvation-shell in an ideal structure, the structure of the coordinated water molecules of the sodium ion and the chloride ion differ in the respect that the waters around the chloride ion are more randomly positioned relative to each other.

With the present model it is possible to obtain an estimate of the coupling between the exchange repulsion and the induction energy, two terms that in standard statistical mechanical models are added to the total interaction energy as if they were independent. Both the lithium and the sodium ion have very small coupling terms, while the fluoride and the chloride ions display greater coupling. The justification for the coupling is that the exchange repulsion changes when the charge distribution

of the ion is perturbed upon polarization; this also explains why the coupling increases in absolute number with the polarizability of the ion.

References and Notes

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