Hydration structure of salt solutions from *ab initio* molecular dynamics

Arindam Bankura, Vincenzo Carnevale, and Michael L. Klein^{a)}

Institute for Computational Molecular Science and Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, USA

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The solvation structures of Na^+ , K^+ , and Cl^- ions in aqueous solution have been investigated using density functional theory (DFT) based Car-Parrinello (CP) molecular dynamics (MD) simulations. CPMD trajectories were collected for systems containing three NaCl or KCl ion pairs solvated by 122 water molecules using three different but commonly employed density functionals (BLYP, HCTH, and PBE) with electron correlation treated at the level of the generalized gradient approximation (GGA). The effect of including dispersion forces was analyzed through the use of an empirical correction to the DFT-GGA scheme. Special attention was paid to the hydration characteristics, especially the structural properties of the first solvation shell of the ions, which was investigated through ion-water radial distribution functions, coordination numbers, and angular distribution functions. There are significant differences between the present results obtained from CPMD simulations and those provided by classical MD based on either the CHARMM force field or a polarizable model. Overall, the computed structural properties are in fair agreement with the available experimental results. In particular, the observed coordination numbers 5.0–5.5, 6.0–6.4, and 6.0–6.5 for Na^+ , K^+ , and Cl^- , respectively, are consistent with X-ray and neutron scattering studies but differ somewhat from some of the many other recent computational studies of these important systems. Possible reasons for the differences are discussed. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4772761>]

I. INTRODUCTION

The properties of solvated ions are of relevance in diverse fields of science ranging from geology to biology with high impact on topical issues such as carbon sequestration, health, and even the viability of ecosystems. Sodium (Na^+) and potassium (K^+) ions are among the most abundant alkali metal ions in aqueous solution and the details of the interactions of these ions with water are crucial for understanding diverse chemical and biological processes.^{1–3} Of note is the selective permeability of ion channels, which is thought to rely on subtle structural differences between the hydration shells of Na^+ and K^+ .^{4–19} The impact of the structural properties of the hydration shell of cations on the conduction mechanism of ion channels is highlighted by the recent observation that Na^+ can bind to the selectivity filter of sodium channels in an almost fully solvated form and that the interactions between the ion and the channel are mediated by water molecules.¹⁰ In particular it has been shown that approximately six oxygens can be found in the first coordination shell of a Na^+ bound to the selectivity filter, of which four are provided by the hydrating waters.²⁰ Despite showing a relatively high degree of mobility, these ligands feature a structure of the ion coordination shell that resembles closely the octahedral geometry of crystal sodium hydrate structures.²¹ In contrast, Zhou *et al.*¹⁷ have shown that in potassium ion channels, the central cavity holds a K^+ ion surrounded by eight ordered oxygen atoms

either from eight water molecules or from a mixture of water and carbonyls. K^+ channels select K^+ over Na^+ by a ratio of 1000:1,^{12–15} whereas the typical Na^+ channels exhibit a Na^+/K^+ selectivity ratio higher than 500:1.^{18,19} These observations raise immediately the hypothesis that the selectivity filters of ion channels are finely tailored to mimic the structure of the first solvation shell of cations. Therefore, the structure of the solvation shell of the Na^+ and K^+ cations in aqueous solutions is of great biological relevance and has been the object a very large number of experimental^{21–32} and theoretical investigations.^{33–49}

In their crystal hydrates, Na^+ is either coordinated to five (trigonal-bipyramidal) or six (octahedral) water molecules, whereas K^+ is hexa coordinated.^{21,22} Over the past several decades, experiments have elucidated details on the hydration shells of ions in aqueous solutions. The coordination number of ions in aqueous solutions, i.e., the number of water molecules populating the first shell of solvation, can be estimated using a variety of techniques including X-ray diffraction, extended X-ray absorption fine-structure spectroscopy (EXAFS), and neutron diffraction. Large variations in the coordination number, ranging from 4 to 6 for Na^+ and 6 to 8 for K^+ were reported. Using X-ray diffraction experiments on concentrated NaOH solution, Megyes *et al.*²⁷ found the coordination number of Na^+ to be in the 4.3–5.3 range. A neutron diffraction study by Soper *et al.*³⁰ and EXAFS study by Glezakou *et al.*³¹ consistently showed a coordination number of 6 ± 0.5 for K^+ ions. More recently, a neutron diffraction study on aqueous NaCl and KCl by Mancinelli *et al.*³² suggests that the coordination number of Na^+ ranges from 4.8

^{a)}E-mail: mlklein@temple.edu.

to 5.3, while the coordination number of K^+ ion is between 4.8 and 6.0.

Neutron diffraction experiments^{50,51} on different ionic solutions have been also carried out to investigate the solvation structure of the Cl^- ion. From these experiments, the coordination number was determined to be within the range 5.3–6.4. For concentrations less than 2 molar, the coordination numbers were found to be in the range 6.2–6.4.

One of the most powerful methods to obtain a realistic description of the equilibrium properties of complex systems with an atomic level of detail is based on the synergy between the accuracy of density functional theory (DFT) within the generalized gradient approximation (GGA) scheme and the ability of MD simulations to adequately explore the relevant configuration space. In the approach, hereafter referred to as *ab initio* MD (or CPMD), the classical equations of motion of the nuclei are solved by computing, for each configuration of the system, the forces acting on each nucleus via electronic structure calculations. This feature allows one to overcome one of the most important limiting factors of typical force-field based MD (hereafter referred to as classical MD), which is the lack of an efficient method to accurately describe highly polarizable systems.

Ab initio MD, and in particular its implementation in the CPMD formalism, has been used to successfully investigate a variety of complex chemical processes occurring in liquids and solids, as well as in biological systems. However, one of the main limitations of this approach stems from the fact that the available exchange and correlation functionals used in DFT are not able to accurately describe dispersion interactions. Dispersion forces can be important in condensed phases and they are expected to have an impact on the structure of the solvation shell of the ions. However dispersion forces are difficult to capture by first principles calculations, as they originate from non-local correlations of the electronic degrees of freedom.

Recently, several theoretical approaches have been developed to add empirical corrections accounting for the effects of dispersion forces into the DFT-GGA scheme, such as pure density (DF)⁵² or non-local van der Waals (vdW-DF) functionals,⁵³ self-consistent polarization density functional theory (SCP-DFT),⁵⁴ semi-empirical C_6R^{-6} potential corrections (DFT-D and DFT-D3),^{55–57} or modifications in the pseudopotentials, as in the dispersion-corrected atom-centered potentials scheme.⁵⁸ Several of these different dispersion correction methods have been shown to improve the agreement between predicted and measured properties.^{59–67}

In particular, vdW-DF has been shown to provide decent agreement with experiments on liquid water. Wang *et al.*⁵⁹ employed the PBE⁶⁸ and revPBE⁶⁹ functionals with the non-local vdW correlation functional proposed by Dion *et al.*⁵³ and obtained equilibrium densities for heavy water at 300 K and 1 bar of 1.13 g/cm³ and 1.02 g/cm³, respectively. The oxygen-oxygen radial distribution function (RDF) of the PBE-vdW water accurately reproduced experimental results while revPBE-vdW water exhibits a much softer structure. Very recently, Zhang *et al.*⁶⁷ carried out NVE *ab initio* MD simulations within the Born-Oppenheimer approximation us-

ing PBE, revPBE, PW86,⁷⁰ and the optimized B88⁷¹ exchange functional with the vdW correlation functional, finding that optB88 yields the best agreement with experimental RDFs.

The empirical correction (D and D3) proposed by Grimme^{55–57} has received considerable attention because of its simple form and the availability of the empirical parameter sets for the most commonly used functionals. The structure of liquid water was investigated by Schmidt *et al.*⁶⁵ using the Grimme correction with the BLYP^{71,72} and PBE functionals at near-ambient conditions. The dispersion correction provided better agreement with the experimental oxygen-oxygen RDF. Consistently, Jonchiere *et al.*⁶⁵ found that structural and diffusive properties of water are better described if the DFT-D3 correction is included when the triple-zeta valence doubly polarized basis set is used in an NVT simulation at 322 K. However, recent investigations performed at different temperatures and/or at constant pressure have highlighted some of the limitations of this approach. Ma *et al.*⁶¹ have shown that neither the BLYP nor the BLYP+D gives a satisfactory estimate of water density. They found that the density of water at 300 K and 1 bar is 1.07 g/cm³ and 0.92 g/cm³, with and without dispersion, respectively. Thus, the error in the estimated density is of the same magnitude in both cases. Yoo *et al.*⁶⁰ used the same correction together with the BLYP functional in a NVT simulation at 385 K and found a severely understructured oxygen-oxygen RDF. Thus, for pure water, there is only a marginal improvement with the Grimme scheme, which seems to exaggerate the effects of dispersion forces.

A possible improvement in the treatment of dispersion forces may be achieved using hybrid functionals, which incorporate a portion of exact exchange from Hartree-Fock theory and have been extensively tested on a large variety of systems. Introduction of exact exchange in *ab initio* simulations of liquid water^{73–76} has been shown to significantly improve the agreement with the experiments for both structure (oxygen-oxygen RDF) and self-diffusion. However, the use of hybrid-functionals within the framework of a plane-waves basis set is a notoriously expensive computation.

Aware of the marginal improvement it offers for pure water and knowing the limitations of the Grimme approach, we nevertheless considered it worthwhile to explore the role of dispersion forces on ionic solutions. To this end, we report our systematic CPMD investigation of the properties of common ions in solution using three popular density functionals (BLYP, HCTH, and PBE). Specifically, we analyze the effects of dispersion forces on the structure and dynamics of the first shell of solvation of the Na^+ , K^+ , and Cl^- ions in aqueous solution. Dispersion interactions having been added by means of the aforementioned atom centered spherical potentials with a R^{-6} radial dependence, as parameterized by Grimme.^{55,56} This DFT-D approach uses the exchange and correlation functional and the empirical correction to describe short- and long-range parts of the electron correlations, respectively. The impact of an accurate description of the short-range part via hybrid-functionals is beyond the scope of the present work and will be the subject of future investigations.

II. COMPUTATIONAL METHODS

A. *Ab initio* molecular dynamics

All of the present *ab initio* MD simulations⁷⁷ employed the CPMD code.⁷⁸ The electronic structure calculations were performed within the GGA of DFT with three different exchange and correlation functionals, BLYP,^{71,72} HCTH,⁷⁹ and PBE,⁶⁸ which have been previously extensively tested on liquid water. We have also carried out additional CPMD simulations (hereafter referred to as BLYP-D, HCTH-D, and PBE-D) using the empirical corrections introduced by DFT-D^{55,56} to investigate the influence of dispersion forces. Only valence electrons were treated explicitly, through the use of the norm-conserving Troullier-Martins pseudopotentials.⁸⁰ The 2s2p state for Na⁺ and 3s3p state for K⁺ were treated as semicore states, effectively including them in the valence. The Kohn-Sham⁸¹ wavefunctions representing all valence electrons were expanded in a plane wave basis set with an energy cutoff of 80 Ry, which was required for an accurate description of the semicore orbitals; the Brillouin zone was sampled at the Γ point only. The CPMD time step δt and fictitious electronic mass μ were fixed at 5 au (0.12 fs) and 700 au, respectively, and we used the deuterium mass for H atoms to effectively decouple the electronic and ionic degrees of freedom, and thereby allow a larger μ and a longer δt . The required adiabatic separation of the electronic and nuclear degrees of freedom was maintained during the simulation for the chosen value of the fictitious mass of the electronic orbitals.

The choice of an appropriate value of the electronic mass parameter is a delicate issue in performing CPMD simulations. However, Grossman *et al.*⁸² have shown that the computed structural properties such as the oxygen-oxygen RDF of deuterated water is very similar when a fictitious mass of either 340 or 740 a.u. is used.

The present system consists of 3NaCl or 3KCl ion-pairs solvated by 122 water molecules, in a periodically replicated cubic supercell with fixed linear dimensions of 15.52 and 15.58 Å, for NaCl and KCl, respectively. This box size was set to reproduce the experimental densities of 1.05 and 1.06 g cm⁻³. The resulting solute concentration is ~ 1.3 M for both the systems. The initial configurations of the CPMD simulations were taken from classical MD simulations, which had been equilibrated for 200 ps at 300 K. In all CPMD simulations, the temperature was kept at the constant value of 315 K using the Nose-Hoover chain thermostat.^{83,84} The elevated temperature was used to avoid glassy behavior⁶² of liquid water observed at lower temperatures. Typically, the CPMD simulations were run for 75 ps, of which the last 60 ps were used for analysis.

Although the BLYP representation of water at 315 K is liquid-like, it is somewhat overstructured and diffuses more slowly compared to experiment.⁸⁵ Nevertheless, this temperature was chosen as the coordination number for the Na⁺ ion⁴¹ gives decent agreement with experiment, whereas it is underestimated at 344 K.³⁹

Classical MD simulations were performed in the NVT ensemble at 300 K using the Gromacs⁸⁶ code. Simulations were carried out using the standard CHARMM force field⁸⁷ and the nonpolarizable TIP4P flexible water model.⁸⁸ To in-

vestigate the effect of polarization on the solvation structure and dynamics of the ions, we have also carried out additional classical MD simulations using the recently developed Drude models of rigid water (SWM4-NDP) and ions.^{89,90} The electrostatic interactions were calculated using the particle mesh Ewald method⁹¹ with a real space spherical cutoff of 7.5 Å and an accuracy threshold of 10⁻⁶. Lennard-Jones interactions were cut off at 7.5 Å. The equations of motion were solved with the velocity Verlet integrator using a time step of 0.5 fs. Trajectories were collected for a total simulated time of 1.5 ns; the last 1 ns was used for analysis.

III. RESULTS AND DISCUSSION

The structural properties of the ionic solvation shells were characterized through RDFs, $g_{\alpha\beta}(r)$, which provide the probability of finding an atom of type β at a distance of r from an atom of type α (relative to that of an ideal gas). The first shell coordination number for water around an ion is a key parameter characterizing the hydration structure. The running coordination number, $n_{\alpha\beta}(r)$ was computed from the corresponding RDFs by integration from zero to r :

$$n_{\alpha\beta}(r) = \frac{4\pi N}{V} \int_0^r g_{\alpha\beta}(r) r^2 dr,$$

where $n_{\alpha\beta}(r)$ represents the number of atoms of type β surrounding atom α in a coordination shell extending from 0 to r , N is the number of β atoms, and V is the volume of the simulation cell.

A. Solvation structure of Na⁺

The Na-O and Na-H RDFs and their corresponding coordination numbers obtained from classical MD and CPMD simulations are shown in Fig. 1. The numerical values for the height (h_{NaO}^{max} and h_{NaH}^{max}) and the location of the first maximum (r_{NaO}^{max} and r_{NaH}^{max}) of the RDFs and the corresponding coordination numbers (n_{NaO} , n_{NaH}) are listed in Table I. Fo-

FIG. 1. Radial distribution functions (upper panels) and their running coordination numbers (lower panels), for Na-O (left) and Na-H (right) obtained from different methods (see text).

TABLE I. Height of the first peak of the RDF $h_{\alpha\beta}^{max}$, positions of the first peak of the RDF $r_{\alpha\beta}^{max}$ (in Å), and coordination number $n_{\alpha\beta}$.

System		BLYP	BLYP-D	HCTH	HCTH-D	PBE	PBE-D	TIP4P	SWM4-NDP
NaCl	h_{NaO}^{max}	4.86	5.79	5.42	5.77	5.01	5.68	7.77	7.68
	r_{NaO}^{max}	2.47	2.55	2.41	2.47	2.37	2.43	2.33	2.34
	n_{NaO}	5.5	6.1	5.4	5.9	4.9	5.8	5.4	5.5
	h_{NaH}^{max}	2.54	2.57	2.75	2.55	2.65	2.60	2.96	2.85
	r_{NaH}^{max}	3.08	3.07	2.95	2.99	2.93	2.95	2.93	2.93
	n_{NaH}	14.0	15.2	13.9	14.7	13.3	15.3	13.6	14.1
KCl	h_{KO}^{max}	3.44	3.88	3.46	3.71	3.54	3.67	4.71	4.93
	r_{KO}^{max}	2.79	2.83	2.81	2.87	2.77	2.86	2.72	2.72
	n_{KO}	5.9	6.9	6.4	7.0	6.1	6.7	6.4	6.7
	h_{KH}^{max}	2.15	2.13	2.21	2.15	2.17	2.01	2.25	2.35
	r_{KH}^{max}	3.31	3.34	3.35	3.39	3.31	3.37	3.28	3.27
	n_{KH}	17.7	19.1	18.1	18.8	17.7	18.9	17.6	18.3
NaCl	h_{ClO}^{max}	2.98	2.77	2.81	2.58	3.13	2.75	4.14	3.11
	r_{ClO}^{max}	3.17	3.17	3.19	3.17	3.11	3.11	3.08	3.12
	n_{ClO}	6.3	6.5	6.6	6.6	5.9	6.2	7.4	7.2
	h_{ClH}^{max}	2.69	2.35	2.44	2.11	2.88	2.39	3.66	2.78
	r_{ClH}^{max}	2.19	2.19	2.21	2.23	2.15	2.15	2.14	2.16
	n_{ClH}	5.5	5.5	5.7	5.5	5.2	5.1	6.3	6.1

cusing on the hydration of the Na^+ ion, we find that at 2.0 Å, the Na-O RDFs starts to rise from zero and reaches a maximum value in the region between 2.3 and 2.5 Å, which corresponds to the first solvation shell of the ion. The position of the second peak is found in the region between 4.4 and 4.5 Å, which corresponds to the second solvation shell. We observe that the first peak is sharp and narrow and is followed by a near-zero first minimum. The position of the first peak of $g_{NaO}(r)$ is 2.33, 2.34, 2.47, 2.41, and 2.37 Å for the TIP4P, SWM4-NDP, BLYP, HCTH, and PBE simulations, respectively. When dispersion forces are included in the CPMD simulation, the location of the first peak of $r_{NaO}(r)$ is shifted towards larger values by nearly 0.1 Å. It is important to mention that these values are in good agreement with recent estimates of the average nearest-neighbor Na-O distance from neutron diffraction²³ and large-angle X-ray scattering (LAXS)²⁸ providing the values 2.40 ± 0.05 and 2.43 ± 0.02 Å, respectively. In particular, the RDFs from the HCTH and PBE-D simulations show the best agreement with the neutron data. Our CPMD simulations are also in reasonable agreement with experiment and other simulations.^{39–45}

The first maximum of the Na-H RDFs is found in the region between 2.95 and 3.1 Å, to be compared with the values of 2.95 and 2.98 Å reported in previous computational studies^{41–43} and in recent experiments.³² The height of the first peak of Na-O and Na-H RDFs are found to be significantly different between the classical and CPMD simulations. The height of the first peak from the CPMD simulations is between 4.8 and 5.8 for Na-O RDF and between 2.55 and 2.75 for Na-H RDF. The Na-O and Na-H RDFs from classical MD show both a more pronounced first peak and a deeper well at the first minimum, suggesting that the pair potentials used in the force-field based approach give rise to a first hydration shell which is more tightly bound to the Na^+ ion. The better agreement between the RDFs from CPMD trajectories and experiments, suggests that the force-field based interactions result in an overly structured shell of neighbors.

For the Na-O and Na-H RDFs the first and the second solvation shells are clearly separated by a deep first minimum. The first minimum of the Na-O RDF, which marks the outer limit of the first hydration shell of Na^+ , is located approximately at 3.2 Å, whereas the first minimum of Na-H RDF is observed approximately at 3.7 Å. The coordination numbers determined by integrating the first peak of the RDF vary considerably among the different models. Integration up to the first minimum (3.2 Å) of the Na-O RDF gives the coordination numbers of 5.4, 5.5, 5.5, 5.4, and 4.9 for the TIP4P, SWM4-NDP, BLYP, HCTH, and PBE MD simulations, respectively. These results, in particular those obtained with the HCTH functional, are in fair agreement with the coordination number of 5.3 estimated from the neutron diffraction on aqueous (1–2 M) NaCl and NaOH solutions.^{27,32}

Our computed coordination numbers are in good agreement with the previous *ab initio* MD simulations of Na^+ ion in water where a coordination number of 5.2 ± 0.1 is obtained for Na^+ ,^{41–45} as well as with the QM/MM simulations of Tongraar *et al.*³⁸ (5.6 ± 0.3). The coordination number estimated here is also somewhat consistent with that obtained from *ab initio* MD simulations by Rempe and Pratt³⁹ (4.6). The AMOEBA polarizable force field of Grossfield *et al.*⁹² gives the coordination number of 6.0 and the other classical polarizable MD simulations gives 5.7⁹³ and 5.6.^{35,45,90} Cavallar *et al.*⁴⁰ have studied the microscopic solvation shell structure of concentrated aqueous solutions (4.8 M) of NaCl using the BLYP exchange and correlation functional, where a coordination numbers of 4.3 was found for Na^+ ion.

When the empirical correction for the dispersion forces is included, the coordination number of Na^+ increases significantly to the values of 6.1, 5.9, and 5.8 for BLYP-D, HCTH-D, and PBE-D, respectively. Comparing the coordination numbers determined using DFT-D with those using DFT, a clear trend is observed: there is consistently an increase by approximately 0.5 for all the exchange and correlation functionals. Overall, the inclusion of the dispersion correction

FIG. 2. Distributions of coordination numbers based on various methods for (a) Na^+ and (b) K^+ , calculated within the first minimum of the Na-O and K-O RDFs, respectively.

results in a broadened first peak of the Na-O RDFs and the coordination number increases to about six. Although this result seems at odds with the coordination number estimated from neutron diffraction,^{27,32} it should be mentioned that recent LAXS experiments,²⁸ as well high level *ab initio* MD simulations⁴⁵ point towards a coordination number of about six.

The average Na-H coordination number computed from our simulations is found to be between 14 and 15, most of the H atoms being from the first solvation shell waters. Although the second solvation shell of waters is less defined than the first, it is composed of 14–15 molecules at a distance ranging between 3.2 and 5.5 Å.

A comparison of the DFT-D results with those from the non-local vdW-DF scheme demonstrates the usefulness of our approach. For NaCl we have also investigated the effect of dispersion forces using a non-local vdW correlation with the PBE functional (vdW-DF⁵³) and find a Na^+ coordination number of 5.7, which is close to our DFT-D result. The first peak height of the Na-O and Na-H RDFs from vdW-DF both show a slightly more pronounced first peak compared to that of DFT-D: $h_{\text{NaO}}^{\text{max}}=5.97$, $r_{\text{NaO}}^{\text{max}}=2.43$, $h_{\text{NaH}}^{\text{max}}=2.87$, $r_{\text{NaH}}^{\text{max}}=3.01$ (see Fig. S-1 in the supplementary material⁹⁴).

It is useful to analyze the solvation structure of an ion by the probability distribution of the coordination numbers. The normalized probability distribution functions of the coordination numbers are shown in Fig. 2. We found that in the *ab initio* simulations the first solvation shell of Na^+ is preferentially populated by 5 or 6 water molecules with the value of $n_{\text{NaO}} = 5$ being the dominant one. However, it should be noted that these two coordination numbers account for only 50%–60% of the configurations of the system. The probability distribution of coordination numbers from DFT-D simulations is found to be non-negligible between 5 and 7, with $n_{\text{NaO}} = 6$ being the most probable number. Coordination of Na^+ ion by 6 waters is within 55%–65% and $n_{\text{NaO}} = 5$ or 7 accounts for about 15%–25% of all coordination states.

In order to analyze the individual contributions to the RDFs, we have calculated partial RDFs for each water molecule populating the first solvation shell. Specifically, for each instantaneous configuration of the system, all water molecules were ordered according to their distances. By av-

FIG. 3. O-M-O angular distribution functions of θ angle in the first solvation shell of Na^+ and K^+ , calculated for all the waters found instantaneously within the first minimum of the Na-O and K-O RDFs, respectively.

eraging over all configurations, the ion-oxygen RDFs for the n th neighbor were calculated (shown in Fig. S-2 in the supplementary material⁹⁴). The influence of the dispersion correction is clearly revealed in these partial distributions plots. For the Na^+ ion, the standard DFT simulation predicts that the first 5 water molecules are at distances $r < 3.2$ Å; only the 6th water molecule has an extremely broad distribution and extends between the first and second coordination shell, which is consistent with a coordination number between 5 and 6. Instead, DFT-D simulations predict that both the 6th and 7th solvent molecules are broadly distributed between the first and second solvation shell. However, the 6th water molecule is mostly localized in the first shell and therefore the average coordination number is approximately 6.

The geometrical arrangement of the water molecules in the first hydration shell can be characterized by the O-Na-O angle distribution for the water molecules in the first solvation shell (Fig. 3). The same distribution is also reported for each subset of configurations with a defined coordination number between $n_{\text{NaO}} = 5$ and $n_{\text{NaO}} = 8$ (shown in Fig. S-3 in the supplementary material⁹⁴). The prominence of the peaks at 90 and 165 for coordination numbers of 5 and 6 indicates that the arrangement of water molecules around the Na^+ ion is consistent with either a distorted square pyramid or distorted octahedron, respectively. In sodium hydroxide hydrate, the Na^+ ion is found to be penta-coordinated with a distorted trigonal bipyramidal geometry.²¹ Such an arrangement is expected to produce distinct peaks with definite relative heights in the O-Na-O angle distribution around the values of 90, 120, and 180, respectively. Analysis of our MD simulation trajectories reveals that only 1% of the configurations are consistent with this angular distribution.

As expected, water molecules in the first solvation shell of the Na^+ ion are oriented such that the oxygen directly coordinates Na^+ , and the hydrogens point away from Na^+ towards the bulk. This arrangement allows these waters to act as both hydrogen bond donors and acceptors. We have investigated the statistics of hydrogen bonds for the water molecules in the

FIG. 4. Radial distribution functions (upper panels) and their corresponding running coordination numbers (lower panels), for the K-O (left) and K-H (right) obtained from the different methods (see text).

first solvation shell by calculating the average number of accepted and donated hydrogen bonds. The average number of hydrogen bonds accepted and donated per water molecule is found to be 0.90 ± 0.05 and 1.90 ± 0.05 , respectively. Thus, considering the three hydrogen bonded waters and the ion, each first solvation shell water is an average four-coordinated.

B. Solvation structure of K^+

The RDFs for the K^+ systems are shown in Fig. 4, together with their running coordination numbers. The peak positions, peak height and coordination numbers are summarized in Table I. The non-negligible values of the RDFs at first minimum indicate that the first solvation shell is not well-defined, and several exchange events take place between the first and second shells. All the simulations show a broader first peak of the RDF compared to the corresponding peak of Na-O RDFs. The first peak in the radial K-O distribution function (Fig. 4) is in the region between 2.75 and 2.80 Å for DFT and shifted towards slightly larger values (2.80–2.85 Å) for DFT-D. We note that comparable values of the average K-O distance have been reported recently from *ab initio* MD simulations.^{44,45,49} Furthermore, these values are in good agreement with the experimental values of 2.73 ± 0.05 Å and 2.81 ± 0.01 Å determined by EXAFS³¹ and LAXS,²⁸ respectively. The X-ray and neutron diffraction³⁰ experiments for KCl aqueous solutions give a K-O distance of 2.8 Å, which is also consistent with our result. The K-O and K-H RDFs from vdW-DF are found to be very similar to those obtained using the DFT-D approach ($h_{KO}^{max}=3.51$, $r_{KO}^{max}=2.83$ Å, $h_{KH}^{max}=2.25$, $r_{KH}^{max}=3.43$ Å, as shown in Fig. S-4 in the supplementary material⁹⁴). The K-O and K-H RDFs from classical MD suggest a more structured solvation shell compared to the CPMD simulations, as already pointed out in previous investigations.^{44–49} *Ab initio* MD simulations, with and without dispersion corrections, produce a more disordered shell of solvation, albeit still slightly more structured than suggested by experimental observations. The second hydration layer spans from 3.5 to 5.5 Å with a maximum at 4.25 Å for

the K-O RDF and from 3.9 to 5.7 Å (maximum at 5.0 Å) for the K-H RDF.

Integrations up to the first minimum of the K-O (K-H) peaks yield average coordination numbers of 6.4 (17.6), 6.7 (18.3), 5.9 (17.7), 6.4 (18.1), and 6.1 (17.7) for TIP4P, SWM4-NDP, BLYP, HCTH, and PBE simulations, respectively. The geometrical cutoff distances of 3.5 and 4.1 Å were used for K-O and K-H, respectively. The coordination number of K^+ increases to 7 when the correction for the dispersion forces is included. However, using the vdW functional we observe a smaller coordination number (6.6). The average coordination number for K^+ is found to be 6 ± 0.5 from EXAFS³¹ and neutron diffraction,³⁰ although a more sophisticated analysis of the neutron data proposed a coordination number of 7.5.⁹⁵

The DFT-D results, as well high level *ab initio* MD simulations⁴⁵ point to a coordination number of about seven for K^+ ion. Whereas DFT models estimate the hydration number to be slightly below (BLYP) or above 6 (HCTH, PBE), which is in relatively good agreement with the previous CPMD simulation of Rowley *et al.*^{45,48} (PW91, 5.96; BLYP, 5.8) and Liu *et al.*⁴⁹ (6.2) but disagree with Ramanianah *et al.*⁴⁶ (6.7). A higher coordination number of 8.3 ± 0.3 and 7.8 ± 0.2 were obtained from the QM/MM and pairwise-additive model simulations by Tongraar *et al.*³⁸ The AMOEBA polarizable model⁹² predicts a coordination number of 7.0. In contrast, the recent polarizable model of Tripp *et al.*³⁵ produces a significantly higher coordination (7.85 ± 0.48). From our CPMD simulations, the most probable number of water molecules in the second hydration shell is around 18.

Recently Liu *et al.*⁴⁹ have investigated the hydration structure and coordination of K^+ ion solvation in water at 300 and 450 K using *ab initio* CPMD. They found that the height of the first peak of the K-O RDF decreases as the temperature is raised from 300 K to 450 K and the second peak of the K-O RDF appears to be washed out at high temperature. The average coordination number of K^+ ion was 6.24 and 6.53 at 300 and 450 K, respectively, which barely differ.

Compared to the sodium, the region between the first and second peak of the K-O RDF shows a larger occupancy of water molecules. As a result, a broad distribution of coordination numbers within the first solvation shell is observed. In the CPMD simulations, the most probable coordination state for K^+ is found between 5 and 8, with the dominant value of 6 accounting for 50% of the configurations. Inclusion of dispersion corrections results in increased coordination numbers, with a preferred value of 7 accounting for 40% of the configurations. Coordination of K^+ ions by 6 or 8 waters is observed in 20%–25% of the configurations, while the coordination numbers 5 and 9 account for about 5% of the total.

For the K^+ ion, the partial RDFs of K-O (shown in Fig. S-5 in the supplementary material⁹⁴) show that the first and second solvation shells are not clearly separated. Waters in the first solvation shell of K^+ are found to be less localized compared to Na^+ . Indeed, while the five closest water molecules are mostly found within 3.5 Å, the 6th, 7th, and 8th waters explore both the first and second solvation shells,

FIG. 5. Radial distribution functions (upper panel) and their corresponding running coordination numbers (lower panels), for the Cl-O (left) and Cl-H (right) obtained from the different methods (see text).

which is consistent with the broad distribution of coordination numbers.

As for sodium, the geometric arrangement of the waters in the first shell was evaluated by looking at the distribution of the O-K-O angles (Fig. 3). The total angular distribution, together with the angular distributions calculated separately for each coordination state ($n_{KO} = 5$ to $n_{KO} = 8$, shown in Fig. S-6 in the supplementary material⁹⁴) do not show any predominant geometric arrangement, suggesting that the first solvation shell of K^+ is more disordered than that of the Na^+ ion.

The oxygen atoms of the water molecules are directly coordinated to the K^+ ion and the hydrogen atoms point towards the bulk. The first hydration shell of the K^+ ion is less rigid than that of the Na^+ ion, allowing each water molecule to accept one hydrogen bond from the neighboring waters.

C. Solvation structure of Cl^- ion

Structural arrangements of waters around the Cl^- ion are characterized by the Cl-O and Cl-H RDFs, and the results obtained from classical MD and CPMD simulations are shown in Fig. 5 (from vdW-DF simulations, see Fig. S-7 in the supplementary material⁹⁴). The pronounced first peak and deep first minimum indicate a highly structured first solvation shell. The Cl-H RDF shows the presence of two peaks, at 2.15 Å and 3.6 Å, respectively. Interestingly, the first maximum of the Cl-O RDF lies in between these two peaks (3.15 Å), indicating that waters in the first shell are oriented in such a way that only one hydrogen atom points towards the Cl^- ion. The main difference between classical and *ab initio* simulations is the distance between the ion and the first solvation shell. Compared to the *ab initio* simulations, the classical one shows a significantly higher peak located closer to the ion for both the Cl-O and Cl-H RDFs. As for the cations, these differences suggest that the pair potentials used in the force-field based approach give rise to an exceedingly tight binding between the ion and the waters in the first shell of solvation.

FIG. 6. Distributions of coordination numbers based on various methods for Cl^- in (a) NaCl (b) KCl systems.

Indeed the distribution of coordination numbers from force-field based MD is consistently shifted toward higher values compared to the *ab initio* results (see Fig. 6).

The coordination number is found to be between 6 and 6.5, and between 5.2 and 5.5 when integration is performed up to 3.8 Å and 2.9 Å, respectively. In contrast to previous CPMD simulations,⁹⁶ these values, specifically the ones from the *ab initio* simulations, are in good agreement with those obtained from neutron diffraction.^{50,51}

D. Structure of the surrounding water

A crucial aspect of ion solvation concerns the interactions between water molecules. Indeed the number of waters occupying the first shell of solvation will ultimately depend on a subtle balance between water-water and water-ion interactions. Although several comparative studies have extensively investigated the structure of bulk water using different functionals in *ab initio* MD simulations,^{60,62–64,82,85,97–104} we have briefly re-examined this issue here by analyzing water-water correlation functions. The short-range structure of liquid water is obtained from OO RDF and information on hydrogen bonding environment can be deduced from the OH correlation function (shown in Fig. S-8 in the supplementary material⁹⁴). We found a sharp peak near 2.8 Å in the RDF of OO and the height of the peak was found to depend on the exchange and correlation functional. The RDF of OH (shown in Fig. S-8 in the supplementary material⁹⁴) shows a first maximum at around 1.0 Å corresponding to the intra-molecular OH covalent bond and the second peak in the region 1.7–1.8 Å, corresponding to water-water hydrogen bonds. The first peak near 1.55 Å in HH RFD represents the intra-molecular hydrogen-hydrogen distance. It is found that the PBE functional induces a more pronounced short-range order than the BLYP and HCTH, possibly resulting from stronger H-bonding interactions between water molecules. As expected, RDFs and average H-bond distances are found to be very similar between NaCl and KCl systems.

E. Residence time

Besides the structural properties, also the dynamics of the system is expected to crucially depend on the different de-

TABLE II. The average residence times (in ps) of water molecules in the first solvation shell.

System	$\tau_{\alpha O}^R$	BLYP	BLYP-D	HCTH	HCTH-D	PBE	PBE-D	TIP4P	SWM4-NDP
NaCl	τ_{NaO}^R	26.8	16.1	16.4	13.6	111.8	22.8	31.7	38.1
KCl	τ_{KO}^R	12.6	8.6	9.8	6.8	21.9	13.2	4.7	10.5
NaCl	τ_{ClO}^R	14.2	7.3	7.9	5.5	39.3	20.8	8.9	18.3
KCl	τ_{ClO}^R	10.8	8.1	10.2	6.2	25.9	10.4	5.2	11.6

scriptions of the ion-water interactions provided by the models analyzed in this work. An important property in this context is the average residence time of a water molecule in the first coordination shell of the ion. We have estimated the mean residence time using the approach proposed by Impey *et al.*¹⁰⁵ We define two residence variables $h(t)$ and $H(t;t^*)$; the value of $h(t)$ is one if the ion-oxygen distance of the ion-water pair is less than a chosen cut-off at time t and it is zero otherwise, while the value of $H(t;t^*)$ is one if the distance remains constantly within the cut-off from $t = 0$ up to time t and it is zero otherwise. An allowance time, t^* is also set in $H(t;t^*)$ to avoid problems arising from the rattling motion of water molecules of the first hydration shell, so that a water molecule that temporarily leaves the solvation shell for a time shorter than t^* is treated as not having left the solvation shell at all. We construct the correlation function

$$S_R(t) = \frac{\langle h(0)H(t;t^*) \rangle}{\langle h(0)^2 \rangle}, \quad (1)$$

where $S_R(t)$ describes the probability that a water molecule, which was in the hydration shell of the ion at time $t = 0$, remains constantly in the hydration shell up to time, t and the associated relaxation time, defined as the residence time, is denoted as $\tau_{\alpha O}^R$, the chosen tolerance time is $t^*=2$ ps.

The computed correlation functions are shown in Fig. 7 and the decay times are reported in Table II. Analysis of the correlation functions shows that the PBE and PBE-D simulations are characterized by the largest relaxation times. The relatively large residence time of the waters in the first solvation shell is consistent with the over-structured character of

the first solvation shell found for the PBE functional when compared to BLYP and HCTH.

F. Effects of dispersion interactions

To further analyze the effects of dispersion interactions, we calculated the interaction energy between the Na^+ and K^+ ions and a water molecule using the three different exchange and correlation functionals. Specifically, we computed the potential energy as a function of the distance between the ion and the water oxygen (PES) in an isolated cubic supercell with fixed linear dimensions of 15 Å. The interaction energy plots (see Fig. S-9 in the supplementary material⁹⁴) show that inclusion of the dispersion correction consistently increases stability of the minimum for all the exchange and correlation functionals by 1.4 ± 0.1 and 1.0 ± 0.1 kcal/mol for the Na^+ and K^+ ions, respectively.

The reference calculations have been performed using a higher-level quantum chemical CCSD(T) method. We find that the Na^+ (K^+) ion-water molecule interaction energies from the PBE and HCTH-D (PBE-D) methods are comparable to the reference CCSD(T) data. For Na^+ , the PBE method predicts 4.90 water molecules in the first shell, in agreement with the recent neutron experiments. In contrast, the HCTH-D and PBE-D methods produces a significantly higher coordination of 5.9 and 6.7 for Na^+ and K^+ ions, respectively.

IV. CONCLUSIONS

We have investigated the properties of the solvation shell of Na^+ , K^+ , and Cl^- ions by means of CPMD simulations. We used three different exchange and correlation functionals (BLYP, HCTH, and PBE) in combination with an empirical correction for dispersion interactions. Importantly, we find significant differences between the *ab initio* and force field based MD simulations, relating to the behavior of waters occupying the first shell of solvation of the ions. Specifically we find the tighter binding between the ions and the surrounding water molecules, in classical MD simulations, is responsible for significant short-range order of solvating waters and is suggestive of an arrangement similar to that found in hydrate crystals. In contrast, *ab initio* simulations (with the exception of those carried out using the PBE functional) reveal a first shell of solvation characterized by less well defined geometric arrangement and a smaller residence time for the water molecules. The present *ab initio* results for ion hydration structure are consistent with available experimental data. The addition of dispersion force causes a consistent increase of the coordination number for both Na^+ and K^+ . The slightly overestimated coordination number results from an increased

FIG. 7. The time dependence of the continuous correlation functions for the escape dynamics of water molecules from the solvation shell of (a) Na^+ in NaCl, (b) K^+ in KCl (c) Cl^- in NaCl, and (d) Cl^- in KCl, respectively.

propensity for the eight coordinated solvation structure. Importantly, this square antiprism geometry of water molecules is highly resemblant of the shell of ligands present in the selectivity filter of potassium channels (see Figs. S-10 to S-13 in the supplementary material⁹⁴ for the different geometries of the solvation shell). Given the hypothesized role of hydration mimicry in determining selectivity, this observation suggests that a proper treatment of dispersion interactions may be crucial for investigating permeation through biological channels. In light of this, we think that the distribution of coordination numbers needs to be further investigated with the use of increasingly more accurate treatments of dispersion interactions. In particular, an interesting issue concerns the possibility that addition of accurate dispersion forces may provide the correct central tendency of the distribution while increasing the population of the four- and eight-coordinated structures. Such increase in the coordination number would entail a somewhat smaller free energy penalty in transferring the ion from solution to the selectivity filter. However, it is important to note that overcoordination in the binding sites could be one of the factors giving rise to selectivity, as shown recently in one of the most logically consistent and quantitatively predictive investigations of ion selectivity.¹⁰⁶ To make further progress in this issue one will need to consider hybrid functionals and path integral simulations to fully characterize the role dispersion interactions. Finally, to objectively assess the performance of different functionals and empirical corrections for dispersion interactions, one will need to complement the structural characterization with a calculation of the solvation free energies of different alkali metal ions.¹⁰³

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