

Overview

The properties of solvated ions are of paramount relevance in a wide range of biological and chemical systems. Na⁺ and K⁺ ions are among the most abundant alkali metal ions in solution and the details of the interactions between these ions and the water molecules in their first shell of solvation are crucial for the understanding of several diverse chemical and biological processes. Of note is the selective permeability of ion channels, which has been shown to rely on subtle structural differences between the hydration shells of Na⁺ and K⁺ ions. Because of this biological relevance, the structure of the solvation shell of the Na⁺ and K⁺ cations in aqueous solution has been the object of extensive theoretical and experimental investigations. Here we use DFT-based Car-Parrinello MD simulations (with and without dispersion corrections) and classical polarizable MD simulations to provide an accurate description of the structure of Na⁺ and K⁺ ions in aqueous solutions.

Calculation Details:

• *Ab initio* molecular dynamics

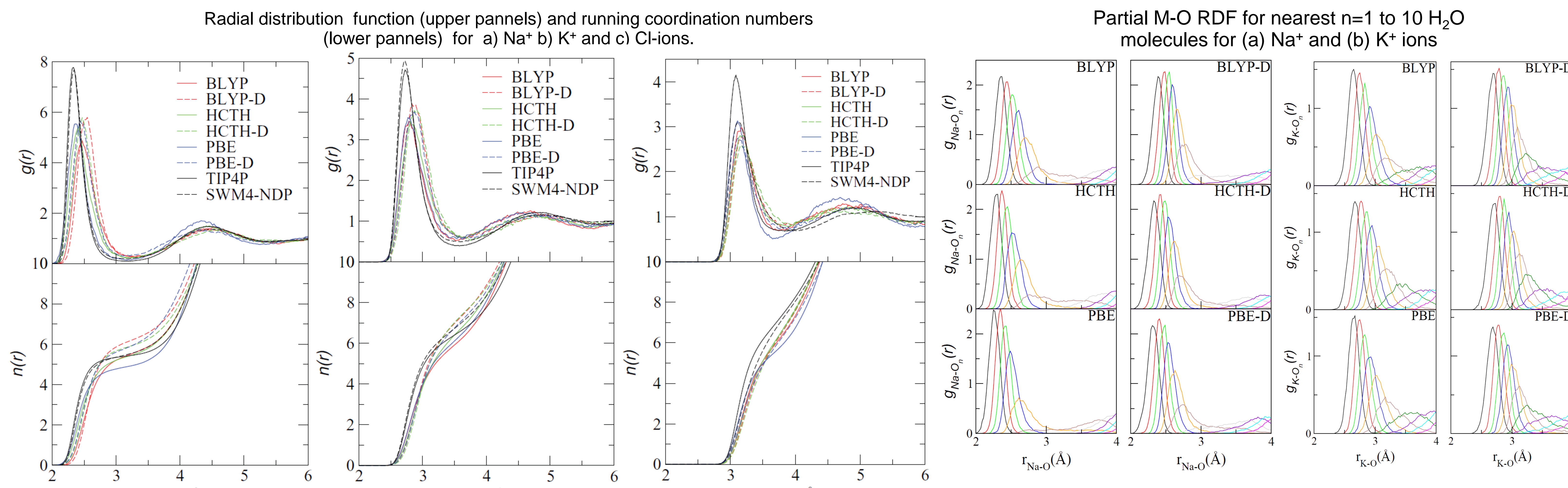
- Car-Parrinello dynamics
- Three NaCl or KCl ion pairs solvated by 122 water molecules
- Cubic supercell, corresponding to experimental ambient density
- Canonical ensemble, T = 315K
- BLYP, HCTH, PBE functional
- Effect of dispersion forces analyzed through the use of an empirical correction to the DFT-GGA scheme proposed by Grimme (DFT-D).
- E_k = 80.0 Ry, Time Step = 5 au, E_{mass} = 700 au
- CPMD simulations were run for 75 ps.

• Classical MD simulations

- Nonpolarizable TIP4P flexible water model and standard CHARMM force field
- Polarizable Drude models of rigid water (SWM4-NDP) and ions.
- Simulation time 1.5 ns

Publication:

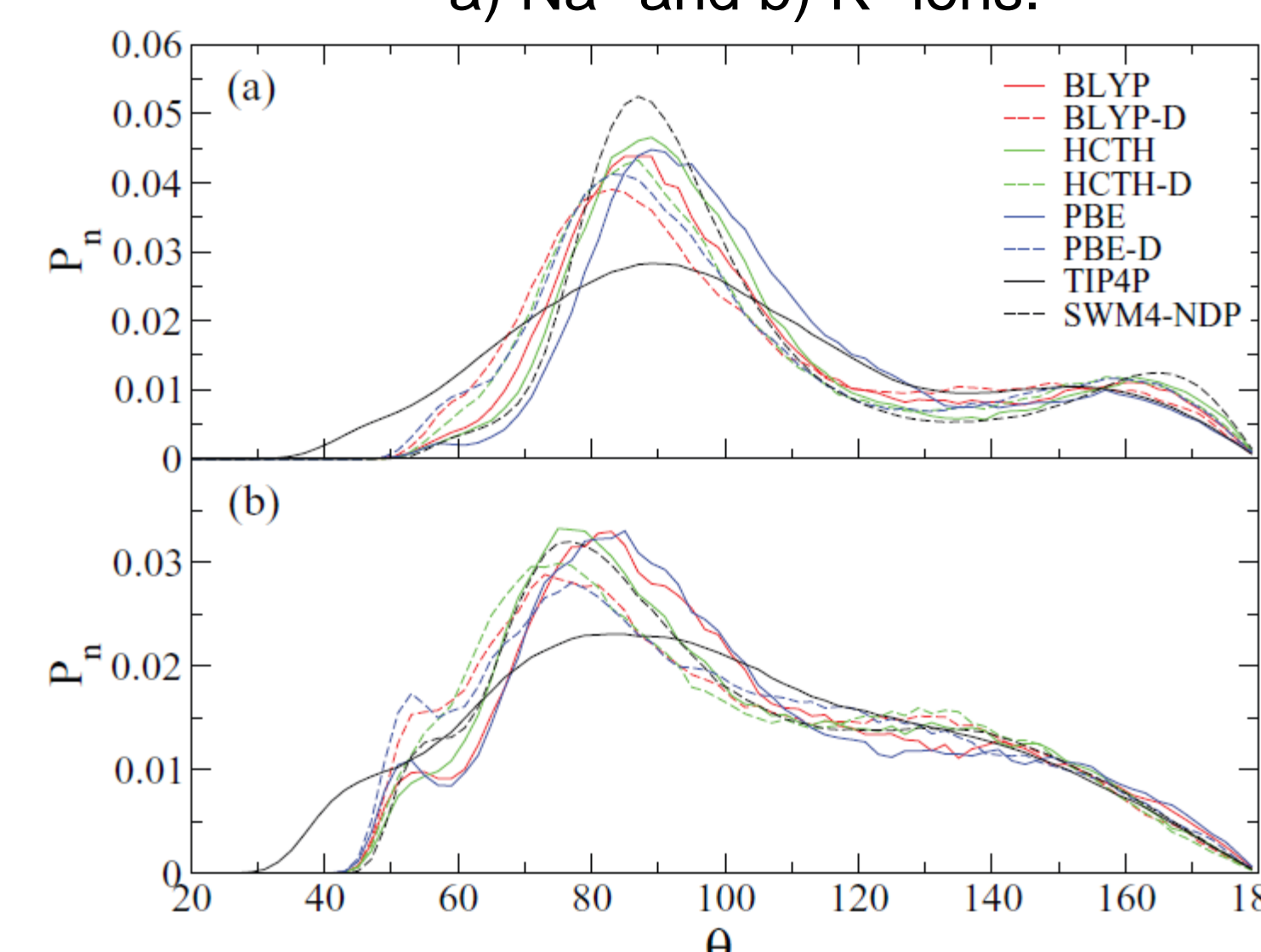
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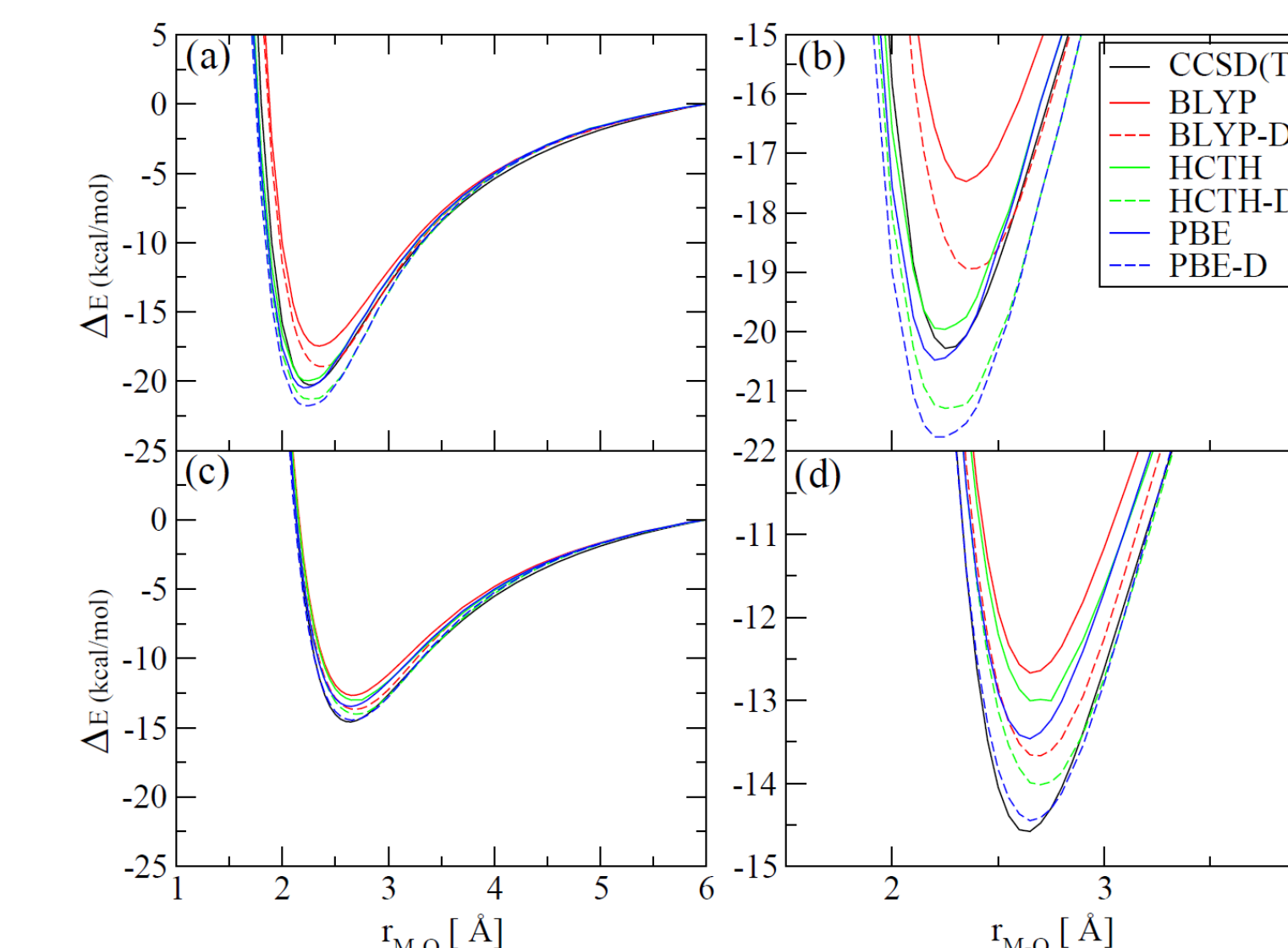
Location of the 1st maximum ($r_{Na-O(max)}$), Coordination number (N_{Na-O}) and average residence time (τ_{KO}^R) for Na⁺, K⁺ and Cl⁻ ions.

	r_{Na-O} (max) (Å)	N_{Na-O}	τ_{NaO}^R (ps)	r_{K-O} (max) (Å)	N_{K-O}	τ_{KO}^R (ps)	r_{Cl-O} (max) (Å)	N_{Cl-O}	τ_{KO}^R (ps)
BLYP	2.47	5.5	26.8	2.79	5.9	12.6	3.17	6.3	12.6
HCTH	2.41	5.4	16.4	2.81	6.4	9.8	3.19	6.6	9.8
PBE	2.37	4.9	111.8	2.77	6.1	21.9	3.11	5.9	21.9
BLYP-D	2.55	6.1	16.1	2.83	6.9	8.6	3.17	6.5	8.6
HCTH-D	2.47	5.9	13.6	2.87	7.0	6.8	3.17	6.6	6.8
PBE-D	2.43	5.8	22.8	2.86	6.7	13.2	3.11	6.7	13.2
TIP4P	2.33	5.4	31.7	2.72	6.4	4.7	3.08	7.4	4.7
SWM4-NDP	2.34	5.5	38.1	2.72	6.7	10.5	3.12	7.2	10.5

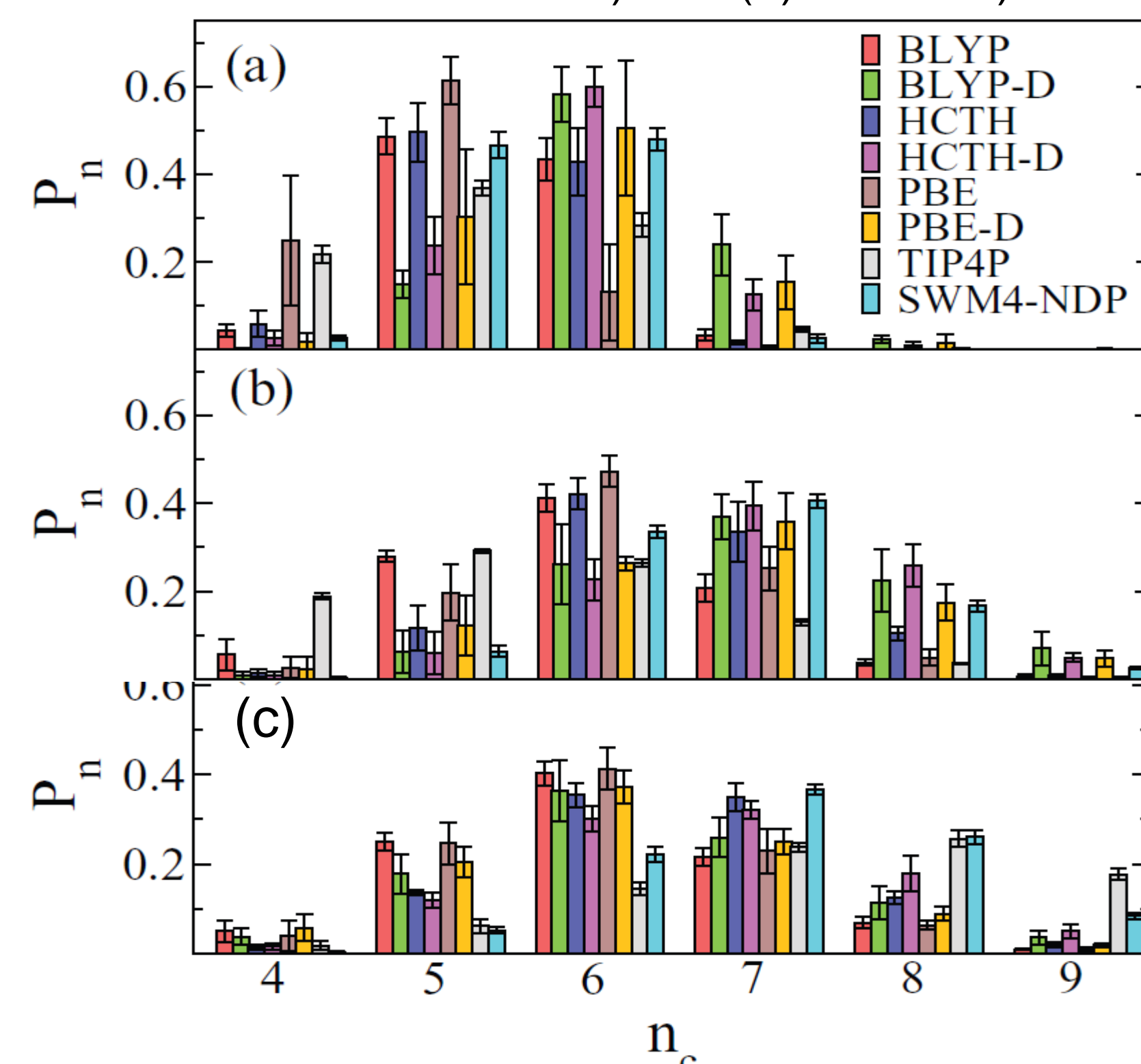
O-M-O Angular Distributions functions of θ angle in the first solvation shell of a) Na⁺ and b) K⁺ ions.



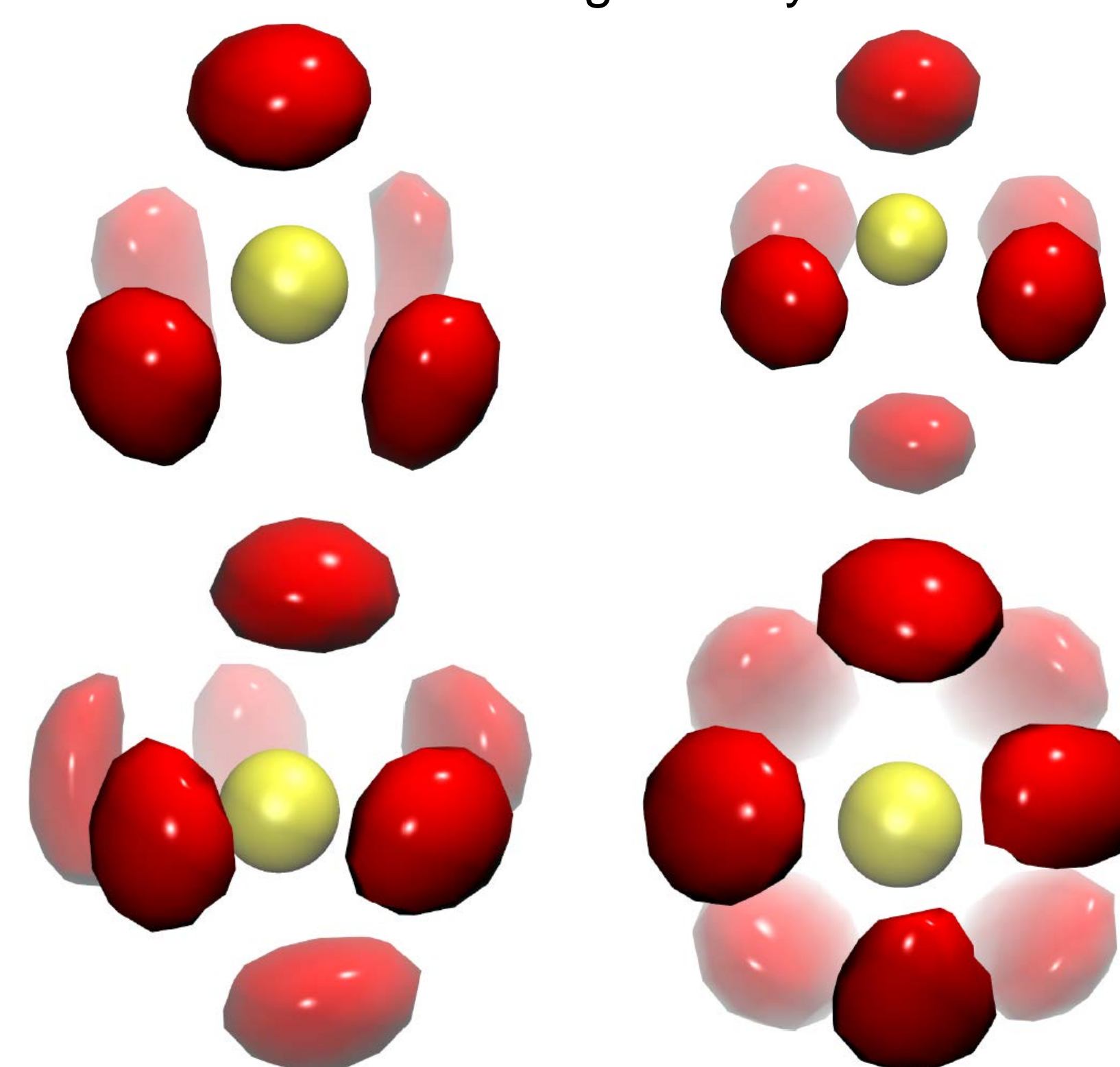
Interaction energy as a function of M-O distance for a) Na⁺ and b) K⁺ ions.



Distributions of coordination numbers based on various methods for a) Na⁺ (b) K⁺ and c) Cl⁻ ions.



Solvation shell geometry of K⁺ ion:



Conclusions

- 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.
- *Ab initio* simulations reveal a first shell of solvation characterized by less well defined geometric arrangement and a smaller residence time for the water molecules.
- The addition of dispersion force consistently increase the coordination number but increase the probability of observing the square antiprism solvation structure present in the selectivity filter of potassium ion channels.
- Proper treatment of dispersion interactions may be crucial for investigating permeation through biological channels.

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