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UNIVERSITY OF CALIFORNIA SAN DIEGO

Many-Body Interactions Dictate the Complex Behavior of Alkali-Metal and Halide Ions in
Aqueous Solutions

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy

in

Chemistry

by

Henry Dionisio Agnew

Committee in charge:

Professor Francesco Paesani, Chair

Professor Tod Pascal

Professor Michael Tauber

Professor Wei Xiong

Professor Joel Yuen-Zhou

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The Dissertation of Henry Dionisio Agnew is approved, and it is acceptable in quality and form for publication on microfilm and electronically.

University of California San Diego

2026

DEDICATION

To my mom and dad. You have always supported my intellectual curiosity throughout my career, whether it was introducing me to robotics, helping me find a summer research program, or even the simple things such as visiting cool science museums with me. These experiences inspired me to pursue my interests in both computers and chemistry and ultimately led me to where I am today. Thank you both for always being there for me.

In Memory of Wenga Agnew.

EPIGRAPH

Whyons?

Me

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LIST OF ABBREVIATIONS

2B	Two-body contribution
3B	Three-body contribution
AIMD	<i>Ab initio</i> molecular dynamics
CCSD(T)	Coupled cluster theory with single and double excitations and perturbative triple excitations
CIP	Contact ion pair
CV	Collective variable
DFT	Density functional theory
DLPNO	Domain-based local pair natural orbital
EXAFS	Extended X-ray absorption fine structure
FF	Force field
GDS	Gibbs dividing surface
JC	Joung and Cheatham force field parameters for ions
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
MBE	Many-body expansion
MB-nrg	Data-driven many-body energy potential
MB-pol	Data-driven many-body potential for water
MB- α	Many-body model for water polarizabilities
MB- μ	Many-body model for water dipoles
MBX	Many-body energy and force calculator software library
MD	Molecular dynamics
MLIP	Machine-learned interatomic potential
NB	N -body contribution
NPT	Constant number of particles, pressure, and temperature ensemble
NVE	Constant number of particles, volume, and energy ensemble
NVT	Constant number of particles, volume, and temperature ensemble
ORCA	Electronic-structure software for DFT and DLPNO CCSD calculations
OPES	On-the-fly probability enhanced sampling
PEF	Potential energy function
PIMD	Path-integral molecular dynamics
PIP	Permutationally invariant polynomial
PLUMED	PLUgin for MolEcular Dynamics software for enhanced sampling
PME	Particle-mesh Ewald
PMF	Potential of mean force
RDF	Radial distribution function
SCF	Self-consistent field
SHAKE	A constraint algorithm for rigid molecules
SSIP	Solvent-shared ion pair
TTM-nrg	Thole-type-model energy potential
vSFG	Vibrational sum-frequency generation
XDM	Exchange-hole dipole moment model

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Chapter 2, in full, has been accepted for publication in *Nature Communications*: **Henry Agnew**, Richa Rashmi, Xuanyu Zhu, Saswata Dasgupta, and Francesco Paesani, “Many-Body Interactions Resolve Halide Distribution at the Air/Water Interface,” *Nat. Commun.*, In Press. <https://doi.org/10.1038/s41467-026-77205-9>. The dissertation author was the primary investigator and author of this paper.

Chapter 3 contains unpublished, ongoing work on many-body ion–ion potentials. Marc Riera Riambau and Xuanyu Zhu were key collaborators in developing the potentials and interpreting the many-body ion–ion interactions presented here. The dissertation author was the primary investigator and author of this work.

VITA

2016–2021 Lead Web Developer, LibreTexts

2020 Bachelor of Science, University of California Davis

2026 Doctor of Philosophy, University of California San Diego

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ABSTRACT OF THE DISSERTATION

Many-Body Interactions Dictate the Complex Behavior of Alkali-Metal and Halide Ions in Aqueous Solutions

by

Henry Dionisio Agnew

Doctor of Philosophy in Chemistry

University of California San Diego, 2026

Professor Francesco Paesani, Chair

Ions in aqueous solution play pivotal roles in many fundamental processes across chemical, atmospheric, and biological systems. Accurately modeling their interactions remains challenging because long-range electrostatics coexist with short-range quantum-mechanical effects. Classical force fields are computationally efficient and scalable, but their simplified functional forms often omit effects such as charge transfer, limiting their transferability beyond the conditions used for parameterization. Machine-learned interatomic potentials (MLIPs) can describe complex local environments, but many lack an explicit treatment of long-range electrostatics and therefore struggle to represent aqueous ionic systems accurately.

This dissertation uses the many-body energy (MB-nrg) framework to model ion–water and ion–ion interactions while retaining physical insight through many-body energy decomposition. First, molecular dynamics simulations of aqueous halides in bulk solution are compared with corresponding results for alkali-metal ions. Fluoride forms a highly structured hydration shell and produces pronounced vibrational shifts relative to the heavier halides, highlighting the importance of many-body effects.

At the air/water interface, a controlled hierarchy of MB-nrg models isolates the roles of pairwise interactions, classical polarization, and explicit short-range many-body effects. Pairwise models exclude all halides from the interface, whereas classical polarizable models overstate their interfacial propensity. The full many-body description instead suppresses adsorption for fluoride, chloride, and bromide and predicts only a shallow free-energy minimum for iodide. Energy decomposition attributes this residual preference to solvent reorganization that offsets ion–water desolvation, while an entropic penalty limits the depth of the free-energy well.

Finally, finite-concentration alkali-metal halide solutions are investigated, where Coulomb interactions complicate the convergence of the many-body expansion. Many-body decomposition of aqueous clusters shows that contributions involving both ions persist to higher body orders than those in water-only or single-ion subclusters. Benchmarks of conventional force fields and MLIPs further demonstrate that accurate short-range interactions must be combined with a physically appropriate treatment of long-range electrostatics. Together, these results establish a systematic route for extending data-driven many-body models from isolated-ion hydration to ion pairing and concentrated electrolyte solutions.

Introduction

0.1 Many-body potential energy functions

The energy, E_N , of a system containing N atomic or molecular monomers can be expressed through the many-body expansion (MBE) [127] as a sum of individual n -body energies, with $n \leq N$, [60]

$$E_N(1, \dots, N) = \sum_{i=1}^N \epsilon^{1B}(i) + \sum_{i < j}^N \epsilon^{2B}(i, j) + \sum_{i < j < k}^N \epsilon^{3B}(i, j, k) + \dots + \epsilon^{NB}(1, \dots, N) \quad (1)$$

where the 1-body energy, ϵ^{1B} , corresponds to the monomer distortion energy for molecular monomers. Higher-body terms are defined recursively as

$$\epsilon^{nB}(1, \dots, n) = E_n(1, \dots, n) - \sum_{m=1}^{n-1} \sum_{1 \leq i_1 < \dots < i_m \leq n} \epsilon^{mB}(i_1, \dots, i_m) \quad (2)$$

Equation 1 provides the foundation for the MB-pol [6, 7, 105, 210, 156, 137] potential energy function (PEF) describing water–water interactions and for the TTM-nrg [5, 161] and MB-nrg [10, 163] PEFs describing ion–water interactions. Both TTM-nrg and MB-nrg ion–water and ion–ion PEFs are built on top of the MB-pol water–water PEF and, in their most general forms, approximate Equation 1 for a single ion interacting with N water molecules as

$$E_N = V^{2B} + V^{3B} + \dots + V^{nB} + V_{\text{elec}} \quad (3)$$

where $n \leq N$ is the body order after which the explicit ion–water terms are truncated, and V_{elec} is an electrostatic term based on a modified version of the Thole model [188] introduced in Ref. 29 and further refined for the MB-pol PEF. [6, 7] V_{elec} represents permanent electrostatics by a sum of Coulomb interactions between smeared partial charges located on the ion and each water molecule (V_{perm}) as well as induced electrostatics (up to dipoles) by an implicit many-body polarization term (V_{pol}):

$$V_{\text{elec}} = V_{\text{perm}} + V_{\text{pol}} \quad (4)$$

In the following, we briefly summarize the theoretical and computational aspects of the TTM-nrg and MB-nrg PEFs. The interested reader is directed to the original publications on TTM-nrg [5, 161] and MB-nrg [10, 163], as well as the MBX software, [162, 59] for a more thorough description and implementation details.

0.1.1 TTM-nrg potentials

TTM-nrg truncates the $V^{n\text{B}}$ ion–water terms in Equation 3 at $V^{2\text{B}}$ and represents the total ion–water interactions as

$$E_N^{\text{TTM-nrg}} = V^{2\text{B}} + V_{\text{elec}} \quad (5)$$

where $V_{\text{elec}} = V_{\text{perm}} + V_{\text{pol}}$ as discussed above and $V^{2\text{B}}$ is expressed as [5, 161]

$$V^{2\text{B}} = V_{\text{short}}^{2\text{B}} + V_{\text{disp}}^{2\text{B}} \quad (6)$$

Here, $V_{\text{short}}^{2\text{B}}$ and $V_{\text{disp}}^{2\text{B}}$ are the total 2-body repulsion and dispersion energies, respectively, between the ion and the oxygen and hydrogen atoms of each water molecule. $V_{\text{short}}^{2\text{B}}$ is calculated as a sum of pairwise-additive Born-Mayer potentials:

$$V_{\text{short}}^{2\text{B}} = \sum_{i=1}^N \left[\sum_{k \in \text{W}_i} A_{Xk} e^{-\delta_{Xk} R_{Xk}} \right] \quad (7)$$

where R_{Xk} is the distance between ion X and atom k of the i th water molecule, W_i . The parameters A_{Xk} and δ_{Xk} are optimized to reproduce 2-body reference energies calculated using coupled-cluster theory with single, double, and perturbative triple excitations [CCSD(T)]. V_{disp}^{2B} is similarly calculated as a sum of pairwise-additive contributions:

$$V_{\text{disp}}^{2B} = \sum_{i=1}^N \left[\sum_{k \in W_i} -f(\delta_{Xk} R_{Xk}) \frac{C_{6,Xk}}{R_{Xk}^6} \right] \quad (8)$$

where R_{Xk} are the same interatomic distances as in Equation 7, $C_{6,Xk}$ are the corresponding dispersion coefficients calculated using the exchange-hole dipole model (XDM), [18, 79, 80] and $f(\delta_{Xk} R_{Xk})$ are the Tang–Toennies damping functions, [187]

$$f(\delta_{Xk} R_{Xk}) = 1 - \exp(-\delta_{Xk} R_{Xk}) \sum_{n=0}^6 \frac{(\delta_{Xk} R_{Xk})^n}{n!} \quad (9)$$

Here, δ_{Xk} are the same fitting parameters as in Equation 7.

0.1.2 (2B)-MB-nrg potentials

The (2B)-MB-nrg potentials are strictly pairwise additive: they truncate the V^{nB} ion–water or ion–ion terms in Equation 3 at V^{2B} and omit the polarization term from the representation of electrostatic interactions:

$$E_N^{(2B)\text{-MB-nrg}} = V^{2B} + V_{\text{perm}} \quad (10)$$

V^{2B} includes a 2-body machine-learned term (V_{ML}^{2B}) along with the same V_{disp}^{2B} ,

$$V^{2B} = \sum_{i=1}^N V_{\text{ML}}^{2B}(X, W_i) + V_{\text{disp}}^{2B} \quad (11)$$

Here, $V_{\text{ML}}^{2\text{B}}$ is expressed as a product of a switching function and a permutationally invariant polynomial (PIP), [27]

$$V_{\text{ML}}^{2\text{B}} = s^{2\text{B}} V_{\text{PIP}}^{2\text{B}} \quad (12)$$

The switching function, $s^{2\text{B}}$, ensures that the contribution from the associated $V_{\text{ML}}^{2\text{B}}$ term goes to zero as the two monomers separate. The linear and nonlinear parameters of $V_{\text{PIP}}^{2\text{B}}$ were optimized using Equation 10 to reproduce a large set of ion–water dimer energies calculated at the CCSD(T) level of theory. [10]

0.1.3 (2B+NB)-MB-nrg potentials

The (2B+NB)-MB-nrg potentials truncate the $V^{n\text{B}}$ ion–water or ion–ion terms in Equation 3 at $V^{2\text{B}}$ but, unlike (2B)-MB-nrg, include many-body effects through the same polarization term used by TTM-nrg:

$$E_N^{(2\text{B}+\text{NB})-\text{MB}-\text{nrg}} = V^{2\text{B}} + V_{\text{perm}} + V_{\text{pol}} \quad (13)$$

$V^{2\text{B}}$ includes a 2-body machine-learned term (Equation 12) and the same $V_{\text{disp}}^{2\text{B}}$ as in (2B)-MB-nrg. The linear and nonlinear parameters of the (2B+NB)-MB-nrg $V_{\text{PIP}}^{2\text{B}}$ term were optimized using Equation 13 to reproduce a large set of ion–water dimer energies calculated at the CCSD(T) level of theory. [10]

0.1.4 (2B+3B+NB)-MB-nrg potentials

The (2B+3B+NB)-MB-nrg potentials adopt the same functional form as the (2B+NB)-MB-nrg potentials but add an explicit $V^{3\text{B}}$ term:

$$E_N^{(2\text{B}+3\text{B}+\text{NB})-\text{MB}-\text{nrg}} = V^{2\text{B}} + V^{3\text{B}} + V_{\text{perm}} + V_{\text{pol}} \quad (14)$$

V^{3B} is fully represented by a 3-body machine-learned term:

$$V^{3B} = \sum_{1 \leq i < j \leq N} V_{ML}^{3B}(X, W_i, W_j) \quad (15)$$

where V_{ML}^{3B} is expressed as a product of a switching function and a PIP, [27]

$$V_{ML}^{3B} = s^{3B} V_{PIP}^{3B} \quad (16)$$

The switching function, s^{3B} , ensures that the contribution from the associated V_{ML}^{3B} term goes to zero whenever any monomer is separated from the trimer. The linear and nonlinear parameters of V_{PIP}^{3B} were optimized using Equation 14 to reproduce a large set of trimer energies calculated at the CCSD(T) level of theory. [10]

0.1.5 Higher-body terms

Higher-body terms can be constructed similarly to the 2B and 3B terms. However, the switching function must be chosen carefully to maintain computational efficiency. This choice determines the configuration space that must be represented in the MB-nrg model and therefore affects the computational cost of both training-set generation and potential evaluation during simulations.

0.2 Chapter Outline

This dissertation is organized into three primary chapters that progress from single-ion hydration in bulk solution to interfacial adsorption and, finally, to ion pairing in solution. Across this progression, the models incorporate increasingly complex many-body interactions.

Chapter 1 focuses on the behavior of halides described by MB-nrg in bulk water, revealing distinct trends in hydration structure, residence times, dipole-moment distributions, and

infrared spectral signatures that reflect variations in ion size, charge density, and polarizability. This chapter, in full, is a reprint of material published in *J. Phys. Chem. B* 2025, 129 (26), 6584–6593. [2] These insights provide a quantitative framework for understanding ion-specific effects in aqueous systems and set the stage for studies of more complex environments, including aqueous interfaces and confined systems. This publication is the second in a series on MB-nrg potentials in bulk aqueous solution and is complemented by companion papers on alkali-metal ions and fluoride, respectively:

- Savoj, R.; **Agnew, H.**; Zhou, R.; Paesani, F. Molecular Insights into the Influence of Ions on the Water Structure. I. Alkali Metal Ions in Solution. *J. Phys. Chem. B* 2024, 128 (8), 1953–1962.
- Rashmi, R.; Savala, B.; **Agnew, H.**; Savoj, R.; Paesani, F. Resolving the Spectral Signatures of Strong Hydrogen Bonding in Fluoride Hydration. *J. Phys. Chem. B* 2025, 129 (28), 7301–7310.

These companion papers provide additional context for comparing alkali-metal ions and halides in aqueous environments. In particular, fluoride promotes uniquely strong and directional hydrogen bonds with surrounding water molecules, leading to substantial spectral shifts and slower water-exchange dynamics than those of the other alkali-metal ions and halides. This distinct behavior is attributed largely to fluoride’s strong three-body interactions with the surrounding water molecules. [153]

Chapter 2 applies these MB-nrg models to the air/water interface. A controlled hierarchy of MB-nrg models isolates the contributions of pairwise interactions, classical polarization, and explicit short-range many-body effects. Decomposition of the interaction energy reveals that both polarization and explicit three-body effects are critical for recovering halide propensities at the interface. This chapter, in full, has been accepted for publication in *Nature Communications*. [1].

Chapter 3 contains ongoing, unpublished work on many-body interactions in aqueous alkali-metal halide solutions. The many-body expansion is used to diagnose the influence of higher-body contributions and to guide the construction of higher-body potentials. The performance of commonly used force fields and machine-learned interatomic potentials in reproducing these ion–ion–water interactions is also assessed.

Chapter 1

Halides in Bulk Aqueous Solutions

1.1 Introduction

Understanding the molecular mechanisms that govern ion hydration is fundamental to a wide range of physicochemical and biological processes. [40] From stabilizing biomolecules and catalyzing enzymatic reactions [118,205,50] to facilitating charge transport in electrochemical systems, [202] ions in aqueous environments play a central role in numerous natural and industrial applications. Hydrated ions also influence atmospheric chemistry, participating in the formation and growth of cloud condensation nuclei. [61, 190, 176, 93] Despite their ubiquity, achieving a predictive understanding of how ions interact with water at the molecular level remains an ongoing challenge, as their hydration structure and dynamics are determined by a delicate balance between ion–water and water–water interactions.

A long-standing approach to describing ion hydration has been the classification of ions as either “structure makers” or “structure breakers” based on their effect on the hydrogen-bonding network of water. [66,41, 101] Based on this classification, small and highly charged ions are thought to strengthen the hydrogen-bond network due to strong ion–water interactions, whereas larger and more diffuse ions are expected to disrupt it. However, experimental measurements using various spectroscopic techniques [35, 180, 172, 55, 197] have challenged the

validity of this simple classification, suggesting a more complex picture of ion-specific effects on water structure.

One of the most debated aspects of ion hydration is the distribution of halide ions at the air/water interface, an issue that has remained unresolved for over a century. Early measurements of surface tension in salt solutions [64] indicated that while cations had little effect, anions influenced surface properties in a manner that followed an inverse Hofmeister series. Classical electrostatic theories, such as those proposed by Wagner [195] and by Onsager and Samaras, [131] predicted that image-charge effects should lead to the depletion of ions at the interface. However, electrostatic potential measurements [53] suggested that larger halide ions, such as bromide and iodide, may in fact be enriched at the interface rather than excluded. Surface-specific vibrational spectroscopic techniques have subsequently been used to probe the air/water interface, leading to conflicting conclusions, with studies supporting either the presence [100] or the absence [154] of larger halide ions in the topmost layers of the water surface. Notably, even successive studies employing advanced vibrational spectroscopies have arrived at differing conclusions, reflecting both the sensitivity of the techniques and the evolving interpretation of ion behavior at the air/water interface. A study on interfacial water dynamics using femtosecond vibrational spectroscopy reported a strong surface propensity of halide ions, [147] whereas a more recent investigation using heterodyne-detected vibrational sum-frequency generation (vSFG) spectroscopy suggested that halide ions primarily reside in a subsurface layer rather than at the outermost interface. [99]

This discrepancy has sparked continued theoretical and computational investigations aimed at elucidating the molecular driving forces governing ion distribution in aqueous environments. Molecular dynamics (MD) simulations have played a pivotal role in advancing our understanding of halide hydration. Early simulations using polarizable force fields (FFs) suggested that bromide and iodide preferentially reside near the surface of water clusters, [142, 143, 144, 44, 145] whereas nonpolarizable FFs predicted that chloride remained in the cluster interior. [184, 185] Subsequent simulations of bulk electrolyte solutions confirmed a trend in which larger halide ions exhibited greater surface propensity, a finding that was consistently observed

with different polarizable models. [83,84,42,43,200] Conflicting results were also reported from *ab initio* molecular dynamics (AIMD) simulations based on density functional theory (DFT), with some functionals predicting lower surface propensities for halide ions than classical force fields. [8] Discrepancies among density functionals have generally been attributed to the limitations of commonly used exchange-correlation approximations in capturing the subtle balance of interactions that govern the properties of water across different phases, [57, 115] an issue now understood in terms of functional- and density-driven errors. [116,39,174,140,138]

Before addressing the additional complexities introduced by interfacial environments, it is essential to first establish a comprehensive understanding of ion behavior in bulk aqueous solutions. Such systems provide a necessary foundation, offering critical insights into hydration structure and dynamics that are indispensable for interpreting more complicated interfacial phenomena. In this context, several simulations using both FFs and DFT-based models have been reported in the literature, focusing on coordination numbers, hydrogen-bonding patterns, and vibrational spectra to assess the extent to which halide ions perturb the surrounding water network. [110,58,89,51,146,54,87,207] However, inconsistencies between different computational methods—particularly in predictions of hydration-shell structure and ion–water interaction strengths—persist even in simulations of ions in bulk water.

A promising strategy for achieving quantitative accuracy in ion hydration modeling is the use of data-driven many-body potential energy functions (PEFs), [139] which accurately account for higher-order interactions beyond the pairwise approximation. Building on the success of the MB-pol PEF for water, [6, 7, 105, 210] our group developed the MB-nrg PEFs, [10, 163] a family of data-driven many-body models for hydrated ions. These PEFs are rigorously derived from the many-body expansion (MBE) of the interaction energy, with individual terms computed using coupled-cluster theory with single, double, and perturbative triple excitations [CCSD(T)]—the current “gold standard” for chemical accuracy in molecular interactions. These PEFs have already been shown to accurately describe ion hydration from small clusters [13, 11, 14, 12, 160, 164] to bulk solutions. [36,37,211,212,171]

In this study, we employ the MB-nrg PEFs for halide ions to provide a comprehensive, molecular-level characterization of their hydration properties in aqueous solution. Through MD simulations, we systematically examine hydration structure, coordination behavior, and the influence of each ion on the surrounding hydrogen-bond network. By correlating structural features with infrared spectral signatures, we gain detailed insights into the local hydrogen-bonding environment around each halide ion. Leveraging the predictive capabilities of the MB-nrg PEFs, we aim to establish a quantitative foundation for understanding ion hydration in bulk water—an essential step toward resolving outstanding questions about ion behavior in more complex interfacial systems.

1.2 Methods

All MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software, [189] interfaced with MBX, a C++ library for MB-pol and MB-nrg PEFs. [162, 59] Specifically, we employed the latest versions of the MB-nrg PEFs for halide–water interactions, as implemented in MBX v1.2. [59] Each system consisted of one halide ion (F^- , Cl^- , Br^- , or I^-) and 277 water molecules (~ 0.2 M concentration) in a cubic box with periodic boundary conditions. The initial configurations were equilibrated for 200 ps in the isothermal-isobaric ensemble (NPT : constant number of particles, pressure, and temperature) at $T = 298$ K and $P = 1$ atm. Afterward, 150 ps-long simulations were performed in the canonical ensemble (NVT : constant number of particles, volume, and temperature) at 298 K, using the average volume obtained from the corresponding NPT simulations. For each ion, ten distinct configurations were extracted at 10 ps intervals from the last 100 ps of the NVT simulations. These configurations were used to generate 10 independent 100 ps trajectories in the microcanonical ensemble (NVE : constant number of particles, volume, and energy).

A global Nosé–Hoover three-chain thermostat with a characteristic time of 0.5 ps controlled the temperature in the NPT and NVT simulations, [104] while a global Nosé–Hoover

three-chain barostat with a characteristic time of 2 ps maintained the pressure in the *NPT* simulations. [104] The velocity-Verlet algorithm [175] was used to propagate the equations of motion with a timestep of 0.5 fs. A cutoff distance of 9.0 Å was applied to short-range nonbonded interactions, while long-range interactions were computed using the particle-mesh Ewald method as implemented in MBX. [178, 179, 162, 59] Unless otherwise specified, structural and dynamical properties presented in the Results section were calculated using data from the *NVE* trajectories.

The MB- μ many-body model was used to calculate the dipole moments of the water molecules. [107] The MB- μ model leverages the rapid convergence of electrostatic properties in aqueous systems, as described by the many-body expansion, [106] and expresses the total dipole moment (μ) of the system as a sum of n -body contributions ($1 \leq n \leq N$). Specifically, μ_{total} is decomposed into explicit machine-learned 1-body (μ^{1B}) and 2-body (μ^{2B}) terms, along with an implicit N -body polarization term (μ^{NB}), which accounts for all higher-order contributions ($3 \leq n \leq N$):

$$\mu_{\text{total}}(1, \dots, N) = \sum_{i=1}^N \mu^{1B}(i) + \sum_{i < j}^N \mu^{2B}(i, j) + \mu^{NB}(1, \dots, N) \quad (1.1)$$

Infrared (IR) spectra were computed within the time-dependent formalism based on the dipole–dipole time autocorrelation function:

$$I_{\text{IR}}(\omega) \propto \int_{-\infty}^{\infty} e^{-i\omega t} \langle \mu(0) \mu(t) \rangle dt \quad (1.2)$$

where μ represents the total dipole moment of the water molecules, calculated using the MB- μ model. Previous studies have demonstrated that MB- μ accurately reproduces both induced and permanent dipole moments of water, enabling simulations of vibrational spectra of water across different phases [107, 108, 183, 28, 155, 70, 109, 114, 113, 112, 111, 152] and various environments. [68, 157, 165, 71, 196, 65, 171, 150]

It has been shown that vibrational spectra of water obtained from quantum MD simu-

lations using centroid molecular dynamics (CMD) [30, 31, 32, 33, 34, 76, 75] and classical MD simulations exhibit similar lineshapes, although the former are redshifted relative to the latter due to the proper inclusion of zero-point energy and anharmonicity. [155] Because of this similarity, and given the additional computational cost of CMD simulations, the analyses in this study are based on classical spectra that have been appropriately redshifted to account for nuclear quantum effects, following previous studies. [107, 109, 155, 70] Specifically, the HOH-bending and OH-stretching vibration bands were shifted by 60 cm^{-1} and 175 cm^{-1} , respectively, to match the corresponding quantum spectra.

The residence time of water molecules was computed using the following time correlation function: [73]

$$n_{1\text{st}}(t) = \frac{1}{N_t} \sum_{n=1}^{N_t} \sum_j P_j(t_n, t; t^*) \quad (1.3)$$

Here, $n_{1\text{st}}(t)$ represents the average number of water molecules that remain in the first shell after a time t elapses. The function $P_j(t_n, t; t^*)$ is equal to one if a water molecule is present in the first hydration shell at both time t_n and $t_n + t$ and does not leave for a time exceeding t^* . Otherwise, $P_j(t_n, t; t^*)$ is equal to 0. $n_{1\text{st}}(0)$ is equivalent to the average coordination number of water molecules within the first hydration shell ($\langle n_{1\text{st}} \rangle$), whereas $n_{1\text{st}}(t)$ corresponds to the number of molecules that reside initially within the first hydration shell and are still there after a time t has elapsed. The parameter t^* is introduced to account for molecules that only transiently leave the first hydration shell. Although the value of t^* cannot be determined unambiguously, in this study t^* was set to 2 ps to remain consistent with the original definition [73] and our analogous study of the hydration properties of alkali metal ions. [171] Given the exponential decay of $n_{1\text{st}}(t)$, the residence time of the water molecules in the first hydration shell of each halide ion ($\tau_{1\text{st}}$) was determined as the time t at which $C(t) = n_{1\text{st}}(t)/\langle n_{1\text{st}} \rangle = 1/e$. It should be noted that the value of the residence time $\tau_{1\text{st}}$ depends somewhat on the choice of t^* , although the trend across the different ions is independent of this choice. For this analysis, eight 2 ns *NVE* simulations were used to calculate the residence time for each ion–water system.

1.3 Results

Figure 1.1(a,b) presents the X^- –O and X^- –H radial distribution functions (RDFs), which describe the spatial correlations between each halide ion (X^-) and the oxygen (O) and hydrogen (H) atoms of the surrounding water molecules, respectively. Complementary insights are provided by the corresponding X^- –O cumulative distribution functions (CDFs) shown in Figure 1.1(c), which report on the coordination number (n_{wat}) as a function of the X^- –O distance for each halide ion. The RDFs reveal a well-defined hydration structure extending up to the third shell for fluoride, whereas it becomes indistinct beyond the first shell in the case of iodide. Chloride and bromide exhibit intermediate behavior, maintaining a distinguishable second hydration shell. This hydration structure is reflected in well-defined coordination numbers for the first and second hydration shells around F^- , while the boundaries between these shells become increasingly diffuse from chloride to iodide. These analyses highlight the balance between ion–water and water–water interactions in the hydration of the four halide ions. Previous MD simulations performed with the MB-nrg PEFs for Cl^- , Br^- , and I^- have shown quantitative agreement with experimental extended X-ray absorption fine structure (EXAFS) spectra, [37,36] demonstrating that the MB-nrg data-driven many-body PEFs accurately capture the local hydration structure of halide ions. As the strength of ion–water interactions decreases and the ion size increases from F^- to I^- , the first peak position of the corresponding RDF shifts to a larger distance and its width

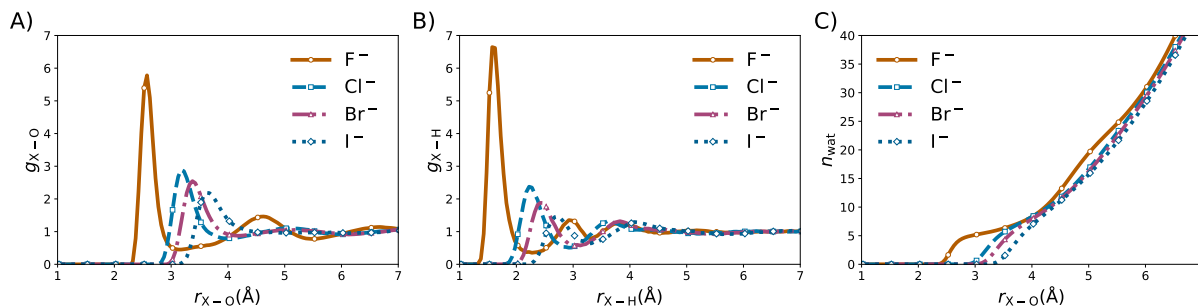


Figure 1.1: (a) Halide–oxygen (g_{X-O}) and (b) halide–hydrogen (g_{X-H}) radial distribution functions calculated from MD simulations carried out with the MB-nrg PEFs for each halide ion. (c) Coordination number (n_{wat}) as a function of the X^- –O distance (r_{X-O}).

broadens. A similar trend was also observed in the hydration structure of alkali metal ions, from Li^+ to Cs^+ , as predicted by simulations with the corresponding MB-nrg PEFs. [171]

Table 1.1 summarizes key structural parameters of the first and second hydration shells, including peak positions, boundary distances, and coordination numbers derived from the RDFs and CDFs in Figure 1.1. As in the case of alkali-metal ions, [171] the MB-nrg PEFs predict structural features that are consistently in agreement with available experimental data, providing further evidence for their reliability across different types of ions. By comparison, a state-of-the-art pairwise-additive model such as Madrid-2019 systematically predicts more compact hydration shells than experimental estimates for all halide ions except F^- , whose first-shell position lies within the experimental range. In this context, the agreement achieved by MB-nrg PEFs is particularly noteworthy, given that these models are derived entirely from first principles, without empirical fitting to experimental observables. Unlike Madrid-2019 and other pairwise-additive models, which are parameterized to match selected experimental data, [208, 24, 25] MB-nrg PEFs retain a high degree of transferability by accurately representing each individual n -body contribution to the underlying Born–Oppenheimer potential energy surface.

Table 1.1 also shows that some commonly used DFT models reproduce experimental structural data at ambient conditions only when simulations are performed at artificially elevated temperatures above 298 K. [97] These discrepancies underscore ongoing challenges in modeling aqueous solutions with DFT models, which tend to overestimate the freezing point of water while underestimating its density. [115] Capturing the delicate interplay between ion–water and water–water many-body interactions, which ultimately governs hydration structure and dynamics, remains a persistent limitation of conventional exchange–correlation functionals. [10, 163, 135, 23, 52] A key source of error in these models arises from their sensitivity to both functional-driven and density-driven errors, [116, 81, 39, 193, 174, 92, 181, 177, 140] with the latter being particularly pronounced for negatively charged ions. Recent advances suggest that density-driven errors in ion–water interactions can be mitigated through density-corrected DFT approaches, [46, 47, 19, 138] offering a promising path toward more accurate and predictive

Table 1.1: Key structural parameters of the first and second hydration shells around each halide ion, as predicted by MD simulations with the MB-nrg PEFs, compared with the corresponding values obtained from MD simulations with the Madrid-2019 FF and various DFT models. Listed are the positions of the first- and second-shell X^- -O peaks, the shell boundaries, and the corresponding oxygen coordination numbers. The second-shell coordination number is cumulative and includes water molecules in both the first and second shells. The experimental values are taken from Refs. 126, 130, 182, 78 and references therein. The Madrid-2019 values are taken from Ref. 24. The DFT values are taken from Refs. 9, 209, 49.

Model	Quantity	F ⁻	Cl ⁻	Br ⁻	I ⁻
Experiment	1st-shell peak position (Å)	2.54–2.92	3.10–3.35	3.14–3.43	3.61–3.76
Experiment	1st-shell coordination number	4–6	4–9	6–10	6–10
MB-nrg (this work)	1st-shell peak position (Å)	2.58	3.18	3.38	3.63
MB-nrg (this work)	1st-shell boundary (Å)	3.13	3.98	4.18	4.63
MB-nrg (this work)	1st-shell coordination number	5.4	8.2	9.0	12.1
MB-nrg (this work)	2nd-shell peak position (Å)	4.63	5.13	5.23	5.83
MB-nrg (this work)	2nd-shell boundary (Å)	5.48	6.08	6.18	6.23
MB-nrg (this work)	2nd-shell coordination number	24.3	30.8	31.7	31.6
Madrid-2019	1st-shell peak position (Å)	2.75	3.03	3.12	3.30
Madrid-2019	1st-shell boundary (Å)	3.40	3.68	3.77	3.86
Madrid-2019	1st-shell coordination number	5.8	6.0	6.1	6.1
Madrid-2019	2nd-shell peak position (Å)	4.61	4.70	4.84	4.98
Madrid-2019	2nd-shell boundary (Å)	5.63	6.00	6.00	6.10
Madrid-2019	2nd-shell coordination number	25.3	29.3	29.1	30.2
BLYP-D (300 K)	1st-shell peak position (Å)	2.62	3.22	3.41	3.75
BLYP-D (300 K)	1st-shell boundary (Å)	3.28	3.94	4.18	4.30
BLYP-D (300 K)	1st-shell coordination number	–	–	–	–
PBE-D3 (390 K)	1st-shell peak position (Å)	2.62	3.12	–	–
PBE-D3 (390 K)	1st-shell boundary (Å)	3.31	3.79	–	–
PBE-D3 (390 K)	1st-shell coordination number	4.70	6.61	–	–
revPBE-D3 (330 K)	1st-shell peak position (Å)	2.65	3.16	–	–
revPBE-D3 (330 K)	1st-shell boundary (Å)	3.37	3.96	–	–
revPBE-D3 (330 K)	1st-shell coordination number	5.32	7.20	–	–
SCAN (330 K)	1st-shell peak position (Å)	2.62	3.16	–	–
SCAN (330 K)	1st-shell boundary (Å)	3.28	3.75	–	–
SCAN (330 K)	1st-shell coordination number	4.88	6.75	–	–
PBE0-D3 (330 K)	1st-shell peak position (Å)	–	3.16	–	–
PBE0-D3 (330 K)	1st-shell boundary (Å)	–	3.85	–	–
PBE0-D3 (330 K)	1st-shell coordination number	–	6.20	–	–

simulations that better align with experimental observations of halide-ion hydration.

Figure 1.2 shows the decay of the coordination function, $C(t) = n_{1st}(t)/\langle n_{1st} \rangle$. The residence time, τ_{first} , is determined by the time at which $C(t)$ crosses the threshold of $1/e$,

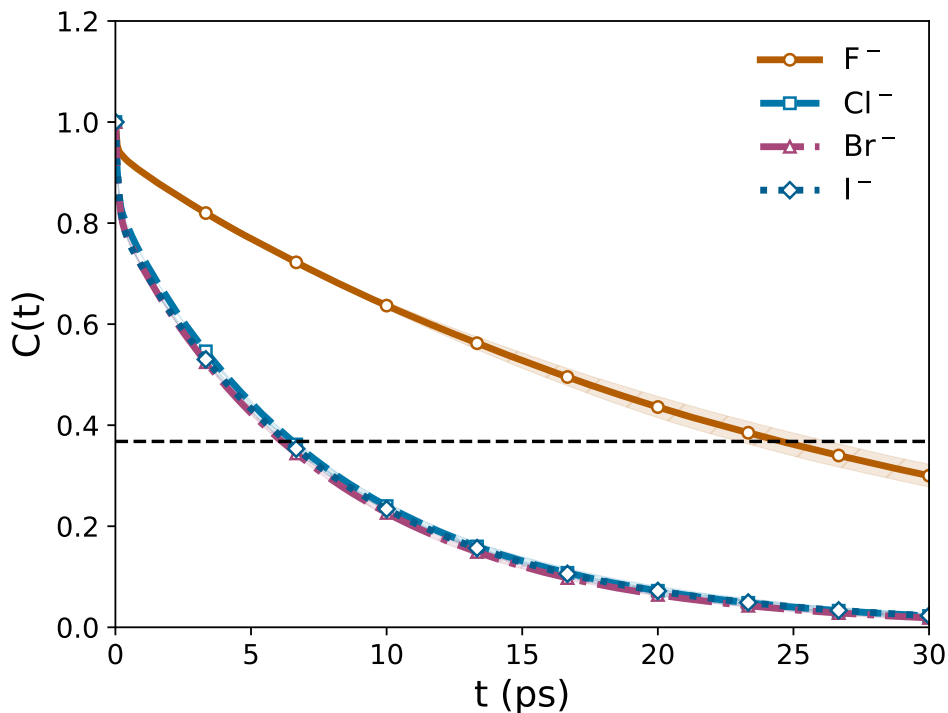


Figure 1.2: Coordination function, $C(t) = n_{1st}(t)/\langle n_{1st} \rangle$, as a function of time. The black dashed line corresponds to $C(t) = 1/e$. The residence time values for F^- , Cl^- , Br^- , and I^- are ~ 24 ps, ~ 6 ps, ~ 6 ps, and ~ 6 ps, respectively.

indicated by the black dashed line in the figure. The residence times of water molecules in the first hydration shells of Cl^- , Br^- , and I^- are relatively similar, suggesting that these ions exhibit comparable abilities to retain water in their first hydration shell despite differences in ionic size.

Fluoride behaves markedly differently, with a significantly longer residence time than Cl^- , Br^- , and I^- . This behavior is explained by its strong hydrogen-bonding interactions with surrounding water molecules, driven by its small ionic radius and pronounced basic character.

A similar trend has been reported for the vibrational lifetime T_1 of an excited O–H stretch of water molecules in the first solvation shell, where $T_1(F^-) \ll T_1(Cl^-), T_1(Br^-), T_1(I^-)$. [90] The vibrational lifetime T_1 of an excited O–H stretch is influenced by hydrogen bonding to the ion, as stronger hydrogen-bond interactions lead to faster relaxation of the vibrational excitation. Therefore, both a shorter vibrational lifetime and a longer residence time imply that fluoride has significantly stronger hydrogen bonds than the other halides.

Interestingly, the residence time of water around F^- (~24 ps) remains considerably shorter than that around Li^+ (> 100 ps), based on analogous MD simulations using the corresponding MB-nrg PEFs for alkali metal ions. [171] The stronger ion–water interactions in the case of Li^+ arise from its smaller ionic radius and higher charge density relative to F^- , allowing it to retain water molecules more effectively in its first hydration shell. [10, 163] Longer residence times are generally associated with more rigid hydration shells and stronger ion–water interactions. This difference may also reflect the orientation of water molecules in the first shell: in the case of Li^+ , the oxygen atoms of water point inward, enabling stronger electrostatic interactions, whereas fluoride, being an anion, forms hydrogen bonds through the water hydrogen atoms, potentially leading to a less rigid hydration structure.

Figure 1.3 shows the distribution of water dipole moments in the first and second hydration shells, as well as in bulk water, for each halide ion. The corresponding average values are reported in Table 1.2. Consistent with previous observations for alkali metal ions, [171] the presence of halide ions alters the dipole moment of surrounding water molecules in a manner that reflects the strength and geometry of ion–water interactions. Water molecules in the first hydration shell of F^- exhibit a pronounced enhancement in dipole moment of approximately 9% relative to bulk water, indicating strong polarization due to the small size and high charge density of the fluoride ion. In contrast, the dipole moments of water in the first shell of Cl^- and Br^- are nearly identical to those in bulk, while a slight decrease of approximately 1% is predicted for I^- . This trend mirrors that observed for alkali-metal ions, where Li^+ —a smaller ion with stronger interactions—induces significantly greater polarization in the surrounding water molecules than do the larger ions in the same group. [171]

Interestingly, the dipole moment of water molecules in the first F^- hydration shell (2.99 D) is lower than that around Li^+ (3.16 D). [171] This difference likely reflects the orientation of water molecules in the hydration shell: in the case of cations like Li^+ , the water dipoles align with their oxygen atoms pointing directly toward the ion, maximizing polarization. In contrast, anions such as F^- form hydrogen bonds primarily through one hydrogen atom, while

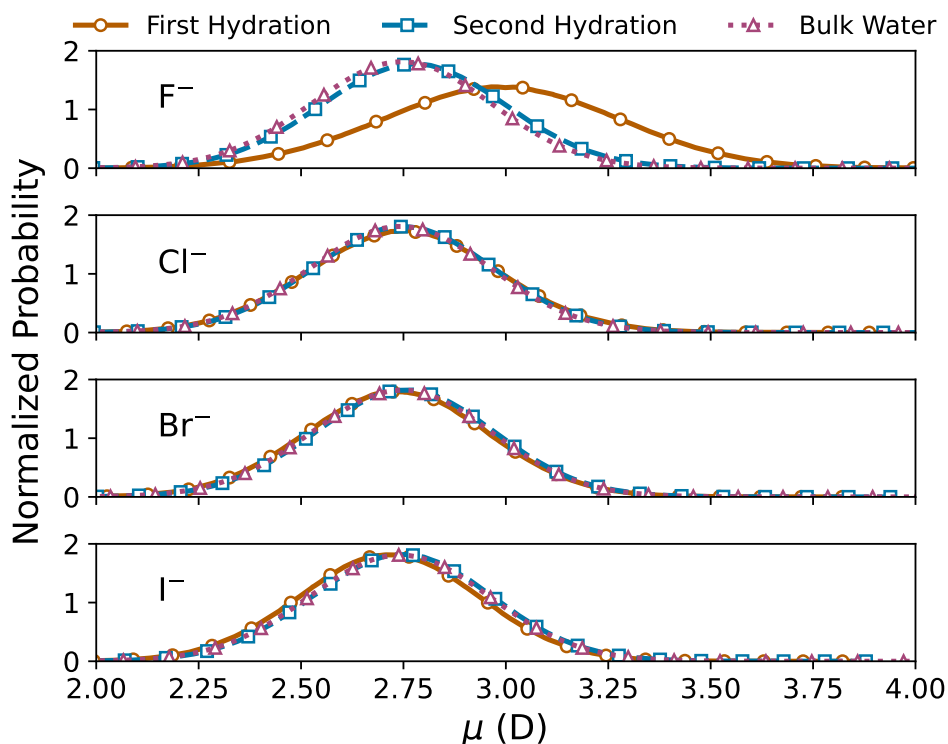


Figure 1.3: Dipole-moment distributions for water molecules in the first and second hydration shells around each halide ion, compared with the corresponding distribution in bulk water. Dipole moments are expressed in Debye (D).

the other O–H bond remains free to interact with neighboring water molecules. This leads to a more asymmetric perturbation of the water dipole and results in a slightly lower net dipole enhancement than that induced by strongly coordinating cations such as Li^+ . These subtle but meaningful differences highlight how the local electric field and water orientation combine to influence the polarization response of water in ion hydration environments.

Table 1.2: Average dipole moment (in Debye) of water molecules in the first and second hydration shells of each halide ion, compared with the corresponding value in bulk water.

Region	F^-	Cl^-	Br^-	I^-
first shell	2.99	2.75	2.74	2.71
second shell	2.77	2.75	2.75	2.75
bulk water	2.74	2.74	2.74	2.74

Figure 1.4(a,b) shows the IR spectra of water molecules in the first and second hydration shells of each halide ion, respectively. The spectrum of the first hydration shell of F^- shows a prominent red shift in the OH-stretching band, indicative of strong hydrogen-bond interactions between fluoride and the surrounding water molecules. In contrast, the stretching bands for Cl^- , Br^- , and I^- are slightly blue shifted relative to bulk water, suggesting weaker ion–water interactions. This distinction reinforces the notion that F^- , due to its small size, high charge density, and pronounced basic character, engages in significantly stronger hydrogen bonding with water than do the heavier halide ions.

Notably, the IR spectrum of water around F^- is even more perturbed than that observed for Li^+ , [171] despite both ions exhibiting high charge densities. However, the average dipole moment of water in the first hydration shell of F^- (2.99 D) is smaller than that for Li^+ (3.16 D), [171] indicating that the pronounced red shift observed in the OH-stretching band of F^- -hydrated water cannot be attributed to electrostatic polarization alone. Instead, it also reflects the contribution of covalent-like interactions between the fluoride ion and nearby water molecules resulting from partial charge transfer along the hydrogen bonds. The ability of F^- to form short,

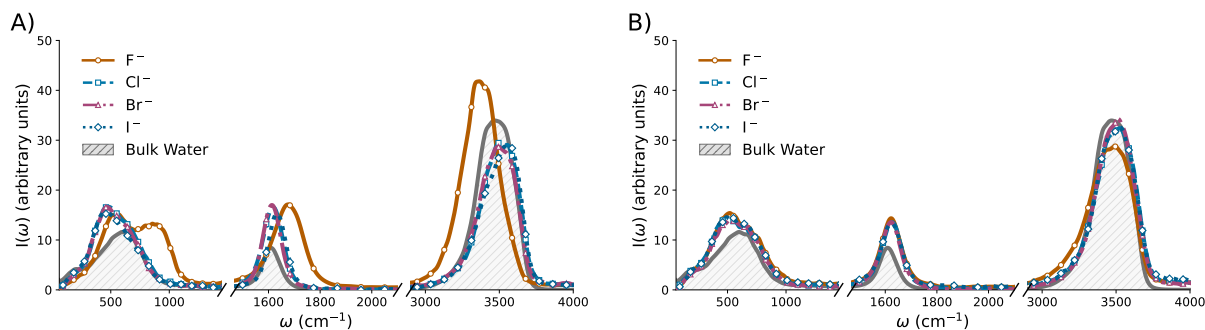


Figure 1.4: Infrared spectra calculated for water molecules located in the first (a) and second (b) solvation shells of each halide ion. All spectra are red-shifted by 60 and 175 cm^{-1} in the bending and stretching regions, respectively, to account for nuclear quantum effects in classical MD simulations of vibrational spectra of water calculated with MB-pol as discussed in refs 107, 109, 155 and 70. The top trace corresponds to the infrared spectrum of liquid water calculated with MB-pol at 298 K. [155]

directional hydrogen bonds—sometimes approaching proton-transfer character—results in significant elongation and weakening of the O–H bonds, which manifests as a strong red shift in the corresponding stretching band.

Additional spectral features support this interpretation. The HOH-bending band for water in the first hydration shell of F^- is blue shifted relative to those for the other halide ions, consistent with stronger hydrogen bonding. Moreover, the libration band for F^- displays a distinct double-peak structure, which is absent in the spectra of Cl^- , Br^- , and I^- . This splitting reflects two different librational timescales arising from the asymmetric environment around water molecules: one O–H bond forms a strong hydrogen bond with F^- , while the other interacts with water molecules in the second shell. Because the $F^- \cdots H-O$ hydrogen bond is stronger and more directional, it restricts rotational motion more effectively, resulting in a higher-frequency librational component. These results underscore the unique hydration characteristics of F^- relative to both heavier halides and alkali-metal ions. A comprehensive analysis of the IR spectrum of fluoride—incorporating simulations across a hierarchy of approximations, from empirical pairwise-additive models such as Madrid-2019 to data-driven many-body PEFs such as MB-nrg—is presented in Ref. 153.

The IR spectra of water in the second hydration shell (Figure 1.4b) are nearly indistinguishable across all four halide ions and closely resemble the IR spectrum of bulk water. However, in the case of F^- , the OH-stretching band remains slightly broader and extends to lower frequencies, suggesting that fluoride’s influence on the hydrogen-bond network persists weakly beyond the first hydration shell. These results are in line with the relatively unperturbed dipole moments of second-shell water molecules and highlight the localized nature of ion-induced effects, which are largely confined to the first hydration shell. The similarity in both structure and vibrational response confirms that the influence of halide ions on water diminishes rapidly beyond the first shell.

1.4 Conclusions

In this study, we have employed MD simulations with MB-nrg data-driven many-body PEFs to investigate the hydration properties of halide ions (F^- , Cl^- , Br^- , and I^-) in aqueous solution. The MB-nrg PEFs, rigorously derived from the many-body expansion of the interaction energy using coupled-cluster reference calculations, enable a highly accurate and transferable representation of ion–water and water–water interactions without relying on empirical fitting to experimental data.

Our results provide a detailed, quantitative description of ion-specific effects on the structure and dynamics of the hydration shells. Fluoride stands out with its strong hydrogen-bonding interactions that lead to well-structured hydration shells, slower water exchange dynamics, enhanced polarization, and significant shifts in vibrational spectra. These effects stem not only from its high charge density but also from covalent-like interactions and partial charge transfer along hydrogen bonds—features that are challenging to capture with both pairwise-additive and polarizable force fields, which rely on classical representations of molecular interactions.

In contrast, chloride, bromide, and iodide exhibit progressively weaker interactions with surrounding water molecules. Their hydration shells are less structured, their IR spectral features remain closer to those of bulk water, and their impact on second-shell water is negligible. These findings highlight the localized nature of halide ion hydration and reinforce the limitations of treating hydration solely through pairwise-additive models.

Importantly, the ability of MB-nrg PEFs to reproduce structural, dynamical, and spectroscopic observables across the halide series with CCSD(T)-level accuracy—without any empirical tuning—highlights their predictive power and transferability. This level of accuracy opens the door to studying more complex aqueous environments, such as aqueous interfaces, confined systems, electrolyte mixtures, and biomolecular hydration.

Looking forward, the insights gained from this study provide a robust foundation for understanding ion–water interactions across multiple length and time scales. Future studies will

extend this framework to examine interfacial behavior, ion pairing, and the effects of competing interactions in heterogeneous or biologically relevant environments. Combined with nuclear quantum effects and improved sampling techniques, the MB-nrg PEFs hold promise for resolving long-standing questions about specific ion effects in chemistry, biology, and beyond.

1.5 Acknowledgements

Chapter 1, in full, is a reprint of the material as it appears in *The Journal of Physical Chemistry B*: **Henry Agnew**, Roya Savoj, Richa Rashmi, Benjamin Savala, and Francesco Paesani, “Molecular Insights into the Influence of Ions on the Water Structure. II. Halide Ions in Solution,” *J. Phys. Chem. B* 2025, 129 (26), 6584–6593. The dissertation author was the primary investigator and author of this paper.

Chapter 2

Halides at the Air/Water Interface

2.1 Introduction

Ions at aqueous interfaces play pivotal roles in diverse chemical and biological processes. [86] For example, the distributions of ions near the air/water interface can influence atmospheric chemistry and climate, [84] while specific ion effects in aqueous environments are key to several biological processes ranging from membrane interactions to protein aggregation. [101] In this context, halide ions offer a stringent test of any theory of specific ion effects because their interactions with water span diverse length scales from local hydration to collective fluctuations of the surrounding hydrogen-bond network. Despite long-standing efforts, fundamental questions persist about how halides partition between bulk water and the air/water interface. [85, 128]

Early experimental studies of electrolyte solutions at the air/water interface revealed pronounced ion-specific signatures. In particular, surface tension measurements showed a strong anion dependence consistent with an inverse Hofmeister trend, with iodide producing the smallest increase and fluoride the largest, [64] while electrostatic potential differences across the air/water interface were found to be more negative for halide solutions than for neat water (with fluoride solutions as an exception). [53] These observations implied an enhanced interfacial presence of

the heavier halides (Br^- and I^-), directly challenging Debye–Hückel theory [48] and classical image-charge arguments advanced independently by Wagner [195] and by Onsager and Samaras, [131] which predict generic ion exclusion.

Advanced experimental probes, including vibrational sum-frequency generation (vSFG) and photoelectron (PE) spectroscopy, have offered rich but sometimes conflicting interpretations: vSFG measurements range from substantial spectral changes consistent with halide accumulation to negligible changes in the free OH peak upon isotopic dilution, [100, 154] while PE studies indicate enhanced near-surface concentrations of Br^- and I^- . [56] More recent vSFG studies have reached opposing conclusions, ranging from reports of extreme surface propensity [147] to models of a stratified interface in which ions occupy subsurface layers beneath an ion-depleted topmost layer. [99]

Molecular dynamics (MD) simulations have yielded model-dependent predictions for halides at the air/water interface. For simple alkali-halide salts, conventional fixed-charge, non-polarizable force fields generally predict little or no halide surface affinity, whereas empirical polarizable models often stabilize the larger, softer anions in the interfacial region. [84, 142, 44, 184, 83, 43, 200, 102]

Ab initio molecular dynamics (AIMD) simulations based on density functional theory (DFT) have added nuance but also variability, [8] as predicted surface propensities can depend sensitively on the chosen exchange–correlation functional, with well-documented functional- and density-driven errors complicating quantitative interpretation, particularly for anions. [39, 140, 138] Combining MD simulations with polarizable force fields with electronic-structure calculations of vertical ionization energies has suggested that changes in extended hydrogen-bond networks can contribute to interfacial stabilization. [141]

Several theoretical models have also been proposed, including dielectric-continuum descriptions of polarizable anions [95] and subsequent extensions that combine ionic polarizability with cavitation and interfacial solvation effects, [96] as well as fluctuation-based descriptions that emphasize interfacial density and electric-field fluctuations, [129, 133] offering complementary

perspectives on how molecular-scale structure informs macroscopic observables.

A quantitative molecular description of halide distributions at the air/water interface requires a water model that is accurate not only in the bulk but also in the highly heterogeneous interfacial environment. In this regard, MB-pol [6,7,105,210] is distinguished by its demonstrated ability to reproduce structural, thermodynamic, dynamical, and spectroscopic properties of water from small clusters to liquid water and ice, [156,137,136] including vapor–liquid coexistence and interfacial properties. [117] Earlier MB-pol studies also reproduced the vSFG spectrum of the air/water interface and its temperature and polarization dependence, [109,114,186,173] and recent work further showed that MB-pol accurately captures polarization-resolved signatures of free OH groups and links them to orientation-dependent local electric fields, providing a realistic description of interfacial heterogeneity. [151]

Recently, data-driven many-body energy (MB-nrg) potentials have extended the MB-pol framework to ions in water by rigorously representing the many-body expansion (MBE) of the energy through machine-learned short-range ion–water n -body terms trained on “gold-standard” coupled-cluster electronic-structure data, combined with physics-based representations of ion–water many-body polarization. [10,163] Within MB-nrg, the short-range machine-learned terms encode quantum-mechanical effects that are absent from classical force fields, including exchange–repulsion, charge penetration, and charge transfer. [23,52] Across the halide series, MB-nrg potentials have accurately reproduced interaction energies, tunneling pathways, and vibrational spectra from the dimer to larger gas-phase clusters, [13,11,14,12] as well as hydration structure, vibrational and X-ray spectra, and free energies in solution. [37,2,153,170]

Leveraging the accuracy and predictive power of MB-nrg potentials, we pinpoint the mechanisms that govern specific halide effects at the air/water interface. By systematically comparing a hierarchy of molecular models, we separate the full ion–water contribution, which encompasses pairwise interactions, permanent electrostatics, many-body polarization, and short-range quantum many-body effects, from the corresponding water cavity/reorganization contribution. This analysis reveals that only I^- retains a slight interfacial preference, with the associated

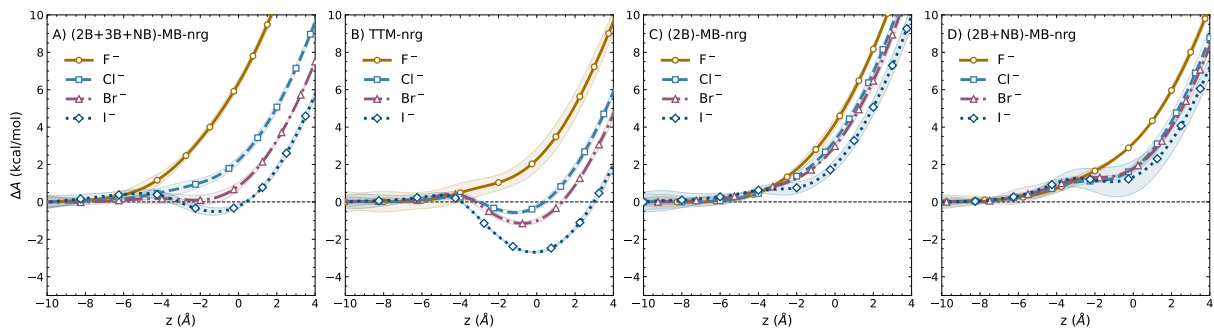


Figure 2.1: Many-body effects suppress halide adsorption. Helmholtz free-energy profiles (ΔA) calculated with the different ion–water potentials along the surface normal referenced to the GDS at $z = 0$. (A) (2B+3B+NB)-MB-nrg; (B) TTM-nrg; (C) (2B)-MB-nrg; (D) (2B+NB)-MB-nrg. Shaded bands denote the 95% confidence interval. Fully many-body (2B+3B+NB)-MB-nrg predicts that only I^- retains an interfacial minimum of order $\sim k_B T$, whereas Br^- , Cl^- , and F^- are not stabilized at the interface. TTM-nrg recovers the strong adsorption of I^- and non-negligible minima for Br^- and Cl^- typical of empirical polarizable force fields. Pairwise additive (2B)-MB-nrg yields repulsive ΔA for all ions, in agreement with classical theories, and adding classical many-body polarization generates only shallow local minima near the GDS that remain marginal compared to bulk hydration.

energetic signature localized in a narrow minimum of the water cavity/reorganization contribution that compensates the ion–water desolvation penalty near the interface.

2.2 Results

2.2.1 A many-body hierarchy of halide surface propensity

To resolve the physical origin of halide surface propensities, we examine a hierarchy of ion–water models built on top of MB-pol. [6,7,105,210,156,137,136] The Thole-type-model energy (TTM-nrg) potentials [5] couple MB-pol with an ion–water polarizable model that includes permanent electrostatics and classical many-body polarization via an extended Thole scheme, [188,29] together with pairwise terms representing repulsion and dispersion interactions, similar to conventional polarizable models used in previous studies. [142,44,184,83,84,43,200]

The MB-nrg potentials [10] refine ion–water interactions through a hierarchy of explicit and implicit many-body terms. [36,37] In the corresponding 2B/3B/NB notation, “2B” denotes

explicit 2-body ion–water terms, “3B” denotes the explicit short-range 3-body ion–water–water term, and “NB” denotes the classical N-body polarization contribution represented through the extended Thole scheme. Accordingly, (i) (2B)-MB-nrg includes a machine-learned short-range 2-body ion–water term, together with permanent electrostatics and pairwise dispersion of the same functional forms used in TTM-nrg; (ii) (2B+NB)-MB-nrg augments (2B)-MB-nrg with the NB many-body polarization term; and (iii) (2B+3B+NB)-MB-nrg further adds the explicit machine-learned 3-body ion–water–water term that captures short-range nonadditive quantum effects.

All potentials were trained on electronic-structure data computed at the coupled-cluster level of theory, including single, double, and perturbative triple excitations, i.e., CCSD(T), [15] which is widely regarded as the “gold standard” for chemical accuracy. [158]

Figure 2.1 reports the Helmholtz free-energy profiles, $\Delta A(z)$, calculated along the surface-normal coordinate for the four halides across the model hierarchy discussed above, with the Gibbs dividing surface (GDS) at $z = 0$. Figure 2.1(A) shows the central result: with the fully many-body (2B+3B+NB)-MB-nrg potentials, only I^- exhibits a shallow interfacial minimum centered at the GDS, whereas F^- , Cl^- , and Br^- remain at or above the bulk reference throughout the interfacial region and are not stabilized at the surface. Thus, in contrast to the pronounced adsorption predicted by previous studies with polarizable force fields, [142,44,184,83,84,43,200] accurately accounting for many-body interactions across the hierarchy of the MBE strongly suppresses interfacial adsorption across the halide series, leaving at most a slight preference of order $k_{\text{B}}T$ for I^- , where k_{B} is Boltzmann’s constant.

To corroborate the origin of the strong interfacial propensity reported with polarizable models, Figure 2.1(B) shows that the polarizable TTM-nrg potential yields a pronounced interfacial free-energy minimum for I^- , smaller but distinct minima for Br^- and Cl^- , and repulsion for F^- . This is the same qualitative trend reported by empirical polarizable force fields. [142,44,184,83,84,43,200] Figures 2.1(A,B) therefore show that the strong adsorption predicted by polarizable models vanishes once n -body ion–water interactions are included with

chemical accuracy, as in the (2B+3B+NB)-MB-nrg potentials. This comparison identifies ion–water many-body effects as the decisive factor controlling halide distributions at the air/water interface.

Figures 2.1(C,D) isolate how pairwise additivity, classical many-body polarization, and explicit short-range many-body effects shape halide behavior at the air/water interface within the MB-nrg hierarchy. When ion–water interactions are described by the purely pairwise-additive (2B)-MB-nrg potentials, all free-energy profiles are repulsive across the interface ($\Delta A \geq 0$). Introducing many-body polarization in the (2B+NB)-MB-nrg potentials generates only shallow local minima near the GDS for Cl^- , Br^- , and I^- , while F^- remains repelled; the bulk state remains thermodynamically preferred in all cases. When explicit short-range 3-body ion–water interactions are further included, as in the (2B+3B+NB)-MB-nrg potentials, the minima for Cl^- and Br^- disappear and the I^- well compresses to a near-thermal depth. These results indicate that the weak interfacial stabilization observed only for I^- emerges from a subtle interplay between the collective response of interfacial water cavity/reorganization effects and short-range, nonadditive ion–water interactions.

The model hierarchy also clarifies connections to classical and continuum theories. The purely pairwise-additive (2B)-MB-nrg description reproduces the generic exclusion predicted by Wagner and by Onsager–Samaras at a dielectric discontinuity. By contrast, combining many-body polarization with conventional pairwise-additive repulsion and dispersion, as in TTM-nrg, yields a pronounced interfacial minimum for I^- and smaller minima for Br^- and Cl^- , qualitatively consistent with the original dielectric-continuum treatment of polarizable anions, in which charge redistribution within a polarizable ion lowers the electrostatic penalty for approaching the dielectric interface. [95] When many-body polarization is integrated with an explicit 2-body ion–water term, as in (2B+NB)-MB-nrg, the resulting profiles are everywhere non-negative, with only shallow near-surface local minima, in qualitative agreement with the extended continuum theory in which ionic polarizability is combined with cavitation and interfacial solvation effects. [96] In this sense, the full (2B+3B+NB)-MB-nrg potential provides a microscopic, many-

body realization of the cavity/reorganization physics that enters continuum descriptions phenomenologically: the explicit short-range 2-body and 3-body ion–water terms do not constitute a cavitation term per se, but instead determine how the surrounding water environment reorganizes and thereby modulate the effective cavity/reorganization contribution. The fact that (2B+NB)-MB-nrg already resembles the extended continuum picture indicates that accurate short-range 2-body ion–water physics captures much of the same net effect represented phenomenologically as cavitation, while the further changes induced by explicit 3-body interactions show that this cavity/reorganization physics is itself modulated by higher-order many-body effects absent from continuum models. Importantly, the disappearance of interfacial minima for Cl^- and Br^- upon inclusion of explicit 3-body interactions highlights a key limitation of continuum approaches, namely the absence of quantum-mechanical many-body effects that ultimately modulate halide surface propensity.

In this context, it is worth noting that the near-thermal interfacial adsorption predicted by (2B+3B+NB)-MB-nrg for I^- is qualitatively consistent with AIMD simulations performed with the revPBE-D3 functional. [8] That agreement should, however, be interpreted cautiously. DFT descriptions of aqueous systems are strongly dependent on the chosen functional [57, 45] and can suffer from both functional-driven and density-driven errors. [39, 177] In particular, analyses of water [174, 46, 140] and halide–water [10, 23, 135, 138] interactions have shown that common density functionals often fail to capture short-range quantum-mechanical effects associated with large intermolecular orbital overlap, including self-interaction, charge penetration, charge transfer, and delocalization errors. These findings have recently prompted a reassessment of the predictive power of widely used DFT models for aqueous systems. [98, 72]

To provide a complementary spectroscopic signature of the many-body hierarchy observed in the Helmholtz free-energy profiles, we calculated the imaginary component of the resonant heterodyne-detected vSFG (HD-vSFG) response, $\text{Im } \chi_{XXZ}^{(2)}(\omega)$, for the same single-halide air/water interfaces and ion–water potentials used in Figure 2.1.

The calculated HD-vSFG spectra, shown in Appendix Figure A.1, are not intended for

direct quantitative comparison with finite-concentration vSFG measurements of electrolyte solutions [100, 154, 147, 99] because the present simulations probe the dilute single-ion limit and therefore exclude counterions, ion–ion correlations, ion pairing, and concentration-dependent interfacial restructuring. Nevertheless, the full (2B+3B+NB)-MB-nrg spectra do not support the extreme-propensity interpretation proposed in Ref. 147, according to which the heavier halides exhibit strong surface propensity. Instead, they are qualitatively consistent with the more recent HD-vSFG measurements of electrolyte solutions reported in Ref. 99, in the sense that they do not show spectral signatures of strong halide accumulation in the topmost interfacial layer, but only an iodide-specific response. The interpretation, however, is different: in the present single-ion limit, the spectra reflect the intrinsic thermodynamic propensity of each halide for the air/water interface, whereas finite-concentration experiments may include additional effects from counterions, ion–ion correlations, and concentration-dependent stratification.

The calculated spectra closely follow the free-energy hierarchy. Consistent with Figure 2.1, TTM-nrg produces a positive hydrogen-bonded O–H feature near 3400 cm^{-1} , accompanied by a decrease in the free O–H peak near 3700 cm^{-1} , for I^- , Br^- , and Cl^- , reflecting the enhanced surface propensity predicted by the polarizable baseline. In contrast, the full (2B+3B+NB)-MB-nrg potential yields an appreciable surface-specific hydrogen-bonded O–H response only for I^- . The (2B)-MB-nrg spectra show no positive hydrogen-bonded O–H feature for any halide ion, whereas the (2B+NB)-MB-nrg spectra show only a weak positive feature near 3400 cm^{-1} for I^- within statistical uncertainty. Thus, the interfacial hydrogen-bonded O–H stretch response mirrors the same many-body hierarchy obtained from the PMFs, providing an independent spectroscopic consistency check of the predicted halide surface propensities.

2.2.2 Desolvation versus water cavity/reorganization

To rationalize the full many-body results in Figure 2.1(A), we decompose the (2B+3B+NB)-MB-nrg Helmholtz free energy as

$$\Delta A = \Delta U - T\Delta S = \Delta U_{\text{ion-water}} + \Delta U_{\text{water-water}} - T\Delta S, \quad (2.1)$$

where $\Delta U_{\text{ion-water}}$ and $\Delta U_{\text{water-water}}$ denote the corresponding contributions to the total configurational energy within the MB-nrg Hamiltonian. Equation 2.1 is therefore used here as a mechanistic decomposition of the total energy along the adsorption coordinate, rather than as a unique thermodynamic partition of the adsorption free energy into independent ion-water and water-water free-energy terms. Within the MB-nrg framework, $\Delta U_{\text{water-water}}$ is obtained by removing the ion from the sampled interfacial water configurations and evaluating the corresponding water energy. It therefore represents a water cavity/reorganization contribution associated with reorganizing the interfacial water environment and accommodating the cavity occupied by the ion at a given position. Conversely, ion-induced polarization and the explicit short-range ion-water 2-body and ion-water-water 3-body terms in the (2B+3B+NB)-MB-nrg potentials are included in $\Delta U_{\text{ion-water}}$. This decomposition is thus distinct from the direct/indirect thermodynamic partition introduced in Refs. 20 and 203.

Figure 2.2 displays $\Delta U_{\text{ion-water}}$, $\Delta U_{\text{water-water}}$, and their sum ΔU for each halide. Across the series, $\Delta U_{\text{ion-water}}$ exhibits a common motif: a broad subsurface minimum located at $z \in [-6, -2]$ Å, with depths clustered around -3 ± 1 kcal mol⁻¹. The curvature of the minimum decreases slightly along the series, i.e., the well becomes broader and softer for the heavier anions. Approaching the interface, $\Delta U_{\text{ion-water}}$ rises as coordinating water molecules are lost and becomes positive near the GDS, reflecting a desolvation penalty that is similar across the halide series.

In sharp contrast, the water cavity/reorganization contribution $\Delta U_{\text{water-water}}$ differentiates the series. For F⁻, it increases nearly monotonically from the bulk and becomes strongly

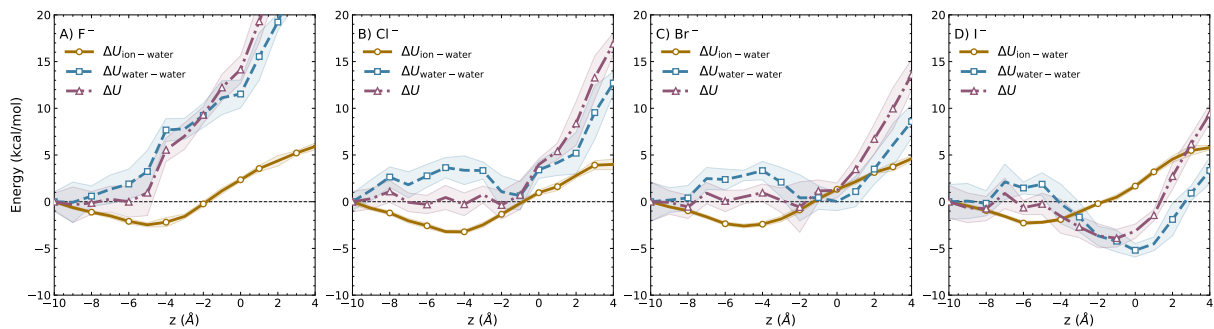


Figure 2.2: Competition between desolvation and water reorganization. Configurational energy decompositions calculated with the (2B+3B+NB)-MB-nrg potentials along the surface-normal coordinate referenced to the GDS at $z = 0$. Shown are the ion–water contribution $\Delta U_{\text{ion-water}}$, the water–water contribution $\Delta U_{\text{water-water}}$, and their sum ΔU for (A) F^- , (B) Cl^- , (C) Br^- , and (D) I^- . Negative values denote stabilization relative to the bulk reference. Shaded bands denote the 95% confidence interval. All ions display a subsurface minimum in $\Delta U_{\text{ion-water}}$. The water cavity/reorganization contribution ($\Delta U_{\text{water-water}}$) differentiates the series: it rises monotonically and becomes strongly positive near the interface for F^- ; it is non-monotonic with a local minimum (higher than the bulk reference value) near the GDS for Cl^- and Br^- ; it exhibits a clear minimum at the GDS only for I^- , which drives a distinct minimum in the corresponding ΔU profile.

positive in the interfacial region (exceeding $+15 \text{ kcal mol}^{-1}$), consistent with the energetic cost of forcing a rigid hydration shell into the hydrogen-bond-deficient topmost layer. For Cl^- and Br^- , $\Delta U_{\text{water-water}}$ is non-monotonic: a subsurface maximum is followed by a shallow minimum near the GDS before rising steeply as the ion protrudes into air. Remarkably, only I^- exhibits a distinct minimum at the GDS, preceded by a subsurface maximum, signaling a transient lowering of the water cavity/reorganization contribution unique to iodide. Consistent with this ion-specific stabilization of the water cavity/reorganization contribution under reduced coordination, quantum dynamical simulations of halide–dihydrate complexes $\text{X}^-(\text{H}_2\text{O})_2$ show that as the halide is varied from Cl^- to I^- , the halide–water hydrogen bond weakens while the intra-dimer water–water hydrogen bond strengthens, providing a minimal undercoordinated motif that mirrors the interfacial environment. [11, 14]

The total configurational energy, ΔU , reflects the balance between ion–water desolvation and water cavity/reorganization contributions. For F^- , Cl^- , and Br^- , cancellation between

$\Delta U_{\text{ion-water}}$ and $\Delta U_{\text{water-water}}$ in the bulk and subsurface regions keeps ΔU near or above zero across the water slab, precluding energetic stabilization at the interface. By contrast, for I^- the desolvation penalty in $\Delta U_{\text{ion-water}}$ near the interface is offset by the concomitant minimum in $\Delta U_{\text{water-water}}$, producing a clear minimum in ΔU centered at the GDS with a depth of approximately -4 kcal mol^{-1} . Within the present many-body decomposition, this minimum should therefore be viewed as the energetic signature of iodide-associated reorganization of the surrounding water environment, rather than as an independent solvent-only driving force.

2.2.3 Microscopic origins of iodide selectivity

Figure 2.3 further resolves the configurational energy, ΔU , into ion–water (top row) and water cavity/reorganization (bottom row) contributions, thereby rationalizing the shapes of $\Delta U_{\text{ion-water}}$, $\Delta U_{\text{water-water}}$, and their sum in Figure 2.2. For all halides, electrostatics dominates the subsurface well in $\Delta U_{\text{ion-water}}$: the permanent term becomes strongly positive as the ion approaches and crosses the GDS (desolvation), whereas induced electrostatics remains favorable throughout. Their sum yields a broad subsurface minimum that shifts modestly toward the GDS from F^- to I^- . The 2-body term, which comprises the machine-learned short-range quantum-mechanical contribution together with dispersion, stabilizes F^- in the subsurface but becomes progressively destabilizing for Cl^- , Br^- , and I^- as first-shell water molecules are lost.

The explicit, machine-learned 3-body ion–water term softens systematically across the series: it is significantly positive for F^- throughout the subsurface and interfacial regions, becomes progressively less repulsive for Cl^- and Br^- , and for I^- develops a shallow stabilizing minimum ($\leq 1 \text{ kcal mol}^{-1}$) in the subsurface. This trend indicates that short-range quantum-mechanical nonadditivity involving the ion and two water molecules strongly penalizes the rigid, tightly coordinated fluoride environment, but is progressively mitigated for the larger, softer halides and can even weakly stabilize iodide. The same trend parallels ion-mediated rearrangement propensities in halide–dihydrate complexes for which quantum dynamics simulations

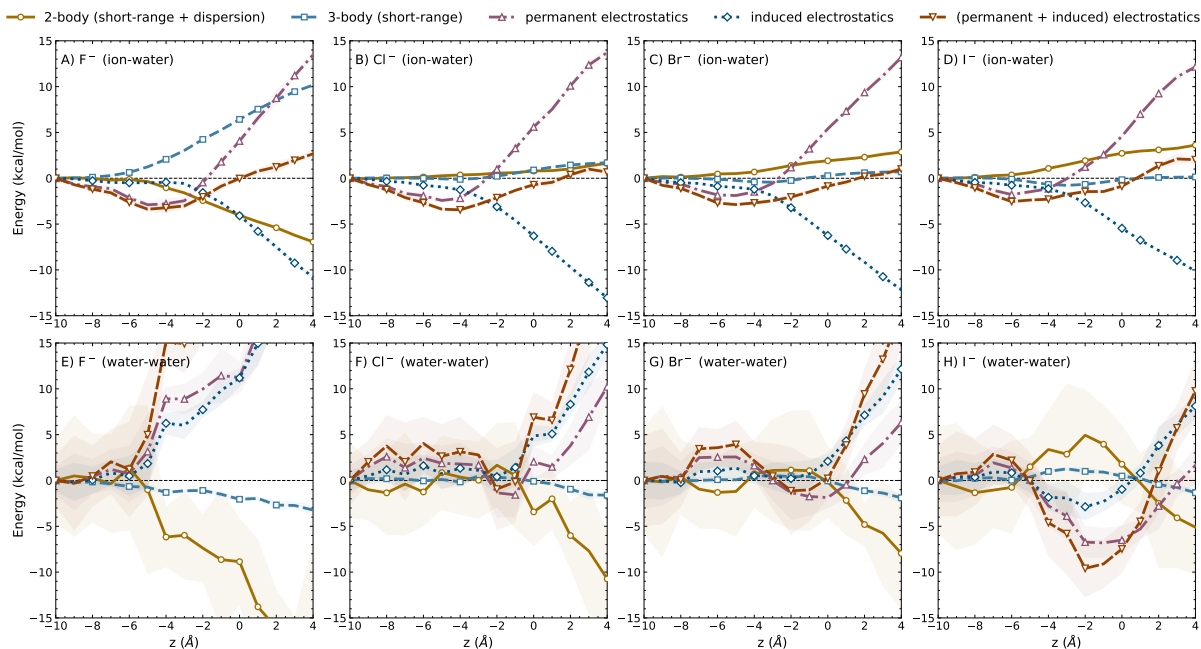


Figure 2.3: Many-body origin of iodide selectivity. Configurational energy contributions calculated with the (2B+3B+NB)-MB-nrg potentials along the surface normal referenced to the GDS at $z = 0$. Top row (A–D): ion–water contributions; bottom row (E–H): water–water contributions. Negative values denote stabilization relative to the bulk reference. Shaded bands denote the 95% confidence interval. Curves resolve 2-body (exchange–repulsion + charge penetration/transfer + dispersion), short-range 3-body, and permanent and induced electrostatics, as well as total (permanent + induced) electrostatics, as indicated in the legends.

showed that the tunneling splitting for the halide–water hydrogen-bond bifurcation increases markedly from Cl⁻ to I⁻, while the splitting for the water–water bifurcation decreases along the same series. [11, 14] Together with the strengthening of the water–water hydrogen bond from Cl⁻(H₂O)₂ to I⁻(H₂O)₂, these cluster-level specific-ion effects are consistent with the reduced short-range 3-body penalty and the selective stabilization of iodide near the interface. This analysis of the ion–water components thus directly rationalizes the subsurface minimum and subsequent rise in $\Delta U_{\text{ion–water}}$ shown in Figure 2.2.

The water cavity/reorganization contribution discriminates the ions even more sharply. For F⁻, water–water electrostatics (both permanent and induced) grows strongly positive on approach to the interface and, although the water–water 2-body term becomes increasingly stabilizing, the net water cavity/reorganization contribution is highly destabilizing near the GDS.

For Cl^- , the water–water 2-body stabilization turns on closer to the GDS but is still offset by a positive electrostatic contribution near the interface. The heavier halides invert this balance: for Br^- and especially I^- , water–water electrostatics becomes negative in a narrow window near the GDS (with I^- also exhibiting a negative induced component), while the water–water 2-body term is transiently positive in the same region, reflecting disruption of optimal pairwise hydrogen bonding by the larger, softer anions. The net result is a distinct minimum in $\Delta U_{\text{water–water}}$ for I^- at the GDS, preceded by a subsurface maximum (Figure 2.2).

Adding $\Delta U_{\text{ion–water}}$ and $\Delta U_{\text{water–water}}$ makes the balance transparent: for F^- , Cl^- , and Br^- , cancellations in the bulk and subsurface keep ΔU near or above zero across the interface, whereas for I^- the narrow water cavity/reorganization minimum near $z \approx 0$ overcompensates the ion–water desolvation penalty, producing a clear minimum in ΔU centered at the GDS. Within the MB-nrg decomposition, this localized water cavity/reorganization minimum is the distinctive energetic signature associated with iodide’s weak interfacial preference.

These trends indicate that iodide is distinguished not by a more favorable ion–water interaction near the interface, but by an ion-specific minimum in the water cavity/reorganization contribution localized at the GDS. In the decomposition of Figure 2.3, this minimum appears explicitly as a narrow lowering of the water–water electrostatic contribution that is absent for F^- and much weaker for Cl^- and Br^- . Within the MB-nrg many-body decomposition, this feature should therefore be interpreted as the energetic signature of iodide-associated reorganization of the surrounding water environment, not as evidence that a solvent-only term independently drives adsorption.

2.2.4 Energy–entropy balance of weak iodide adsorption

Finally, Figure 2.4 resolves the Helmholtz free energy across the water slab into its energetic (ΔU) and entropic ($-T\Delta S$) components (Equation 2.1). For F^- , Cl^- , and Br^- , ΔU remains near or above the bulk reference throughout the interfacial region, while the entropic contribu-

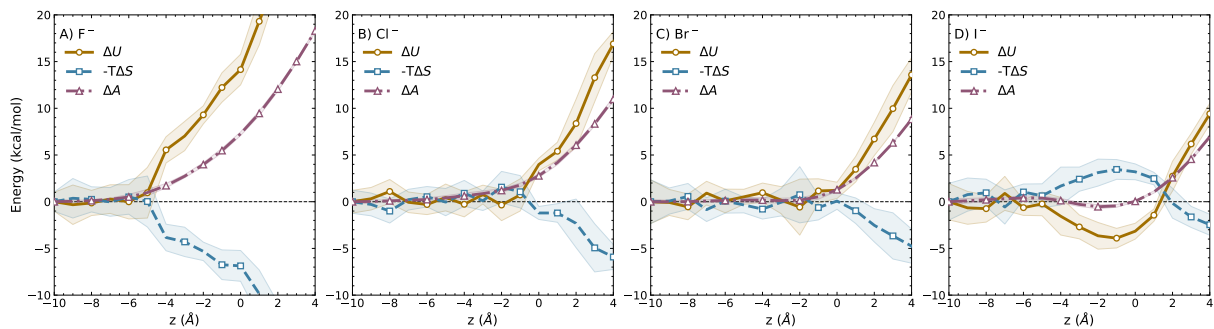


Figure 2.4: Energy–entropy balance limits iodide adsorption. Free-energy decompositions calculated with the (2B+3B+NB)-MB-nrg potentials along the surface-normal coordinate referenced to the GDS at $z = 0$. Helmholtz free energy ΔA is decomposed into the configurational (potential) energy ΔU and the entropic contribution $-T\Delta S$ for (A) F^- , (B) Cl^- , (C) Br^- , and (D) I^- . Negative values indicate stabilization relative to the bulk reference. Shaded bands denote the 95% confidence interval. For F^- , Cl^- , and Br^- , ΔU becomes positive near the interface and dominates over the entropic term, yielding $\Delta A \geq 0$ across the interfacial region. For I^- , a distinct minimum in ΔU at the GDS is partially offset by an entropic penalty ($-T\Delta S > 0$), compressing the net free-energy well to a shallow minimum of order $k_{\text{B}}T$ near $z = 0$.

tion provides only modest modulation near the GDS. Consequently, $\Delta A \geq 0$ across the interface for these ions.

Iodide exhibits a distinct thermodynamic balance. As established in Figure 2.2, ΔU for I^- develops a clear minimum at the GDS, associated within the MB-nrg many-body decomposition with a favorable water cavity/reorganization contribution near the GDS, while $-T\Delta S$ is positive in the same region, indicating an entropic penalty for placing I^- at the surface. The partial cancellation between this energetic gain and the opposing entropic cost compresses the net free-energy well to a shallow minimum of order $k_{\text{B}}T$.

This energy-driven yet entropy-opposed stabilization is qualitatively consistent with previous thermodynamic analyses of interfacial ion adsorption, which likewise found concurrent energetic stabilization and entropic penalty near the interface. [129, 133] At the same time, the present results do not require assigning the entropy penalty specifically to capillary-wave suppression. Rather, within the MB-nrg decomposition, they indicate that iodide’s weak surface preference reflects a localized energetic stabilization associated with interfacial solvent reorganization, together with an opposing loss of interfacial configurational freedom. This interpreta-

tion is also consistent with thermodynamic descriptions that treat adsorption-induced changes in water–water interactions as part of the collective solvent response to the ion, rather than as an independent solvent-only driving force. [20, 203] The modest entropic modulation for Cl^- and Br^- , together with the localized energetic gain unique to I^- , is also consistent with quantum simulations of halide–dihydrate complexes showing that undercoordinated topologies permit ion-specific rearrangements most readily for the softer halides. [14]

The present many-body analyses performed within the MB-nrg framework thus suggest a middle-ground picture of halides at the air/water interface.

Because the present calculations probe the dilute single-ion limit, they are not directly comparable to finite-concentration measurements and simulations, nor can the resulting PMFs be directly converted into surface-tension increments for finite-concentration electrolyte solutions. Through the Gibbs adsorption equation, electrolyte surface tensions depend on the surface excess of the electroneutral salt and therefore require both cation and anion distributions, ion–ion correlations, possible ion pairing, and concentration-dependent interfacial restructuring. The shallow iodide minimum found here should therefore be interpreted as an intrinsic single-ion propensity that can reduce the surface-tension increment of alkali-metal iodide solutions relative to corresponding salts of less surface-active halides, rather than as evidence for a negative surface-tension increment of alkali-metal iodide solutions. Consistent with this interpretation, NaI solutions experimentally increase the surface tension with concentration, but less strongly than NaCl solutions. [77] Within this single-ion scope, the present results do not indicate either the extreme surface propensity suggested by early polarizable-model simulations [84] and inferred from some vSFG measurements, [147] or the ion-depleted topmost interfacial layer inferred in more recent stratification analyses. [99] Instead, they are most consistent with modest iodide surface activity, while Br^- and Cl^- remain thermodynamically bulk-favored. In this sense, the present findings remain broadly consistent with theoretical descriptions that incorporate ionic polarizability and cavitation [95, 96] and are qualitatively compatible with photoelectron evidence for near-surface enrichment of the heavier halides. [56]

2.3 Discussion

We have shown that halide distributions at the air/water interface are controlled by a delicate balance between short-range ion–water interactions, which are quantum mechanical in origin, and water cavity/reorganization effects at the interface. Using data-driven many-body MB-nrg potentials that reproduce ion–water and water–water interactions with chemical accuracy across length scales, we analyzed a systematically controlled hierarchy of ion–water models. Within this hierarchy, purely pairwise-additive interactions exclude all halides, consistent with Wagner and Onsager–Samaras image-charge arguments, whereas classical polarization combined with conventional repulsion and dispersion over-stabilizes the heavier halides, as in empirical polarizable force fields. The full (2B+3B+NB)-MB-nrg potentials instead yield an intermediate regime in which interfacial stabilization is strongly suppressed for F^- , Cl^- , and Br^- , and reduced to a near-thermal minimum for I^- .

Within the MB-nrg decomposition, I^- is distinctive because a narrow minimum in the water cavity/reorganization contribution at the GDS offsets the ion–water desolvation penalty in the configurational energy. The resulting free-energy well nevertheless remains shallow because this energetic gain is opposed by the entropic cost of interfacial structuring. In this way, our results reconcile the qualitative insights of polarizable-anion continuum models with the more restrictive classical image-charge picture: halide surface propensity is not a simple consequence of ionic softness, but the outcome of a finely balanced many-body competition between ion–water interactions and collective water reorganization. The MB-nrg framework therefore provides a rigorous and mechanistically transparent benchmark for interpreting surface-sensitive measurements.

2.4 Methods

Following prior MB-pol simulations of the air/water interface, [117, 109, 114, 186, 173, 151] all MD simulations were performed using a slab geometry consisting of 511 water molecules and a single halide ion in a simulation box of dimensions $20 \times 20 \times 100 \text{ \AA}^3$. Simulations were performed at 298 K in the canonical (*NVT*, i.e., constant number of particles, volume, and temperature) ensemble with the MBX library [162, 59] for data-driven many-body potentials, interfaced with LAMMPS [189] and PLUMED. [192] The velocity-Verlet algorithm [175] was used to propagate the equations of motion with a time step of 2.0 fs. The temperature was controlled with a global Nosé–Hoover chain of three thermostats with a characteristic time of 1 ps. [104] The initial configurations were taken from previous MB-nrg simulations and further equilibrated using the corresponding TTM-nrg or MB-nrg potential for at least 100 ps. All results presented in the manuscript were obtained by constraining the water geometry with SHAKE [169] to the average MB-pol geometry obtained from quantum path-integral molecular dynamics (PIMD) simulations, [105] corresponding to an OH bond length of 0.988 Å and an HOH bond angle of 105.5°.

The potentials of mean force (PMFs) were calculated from MD simulations performed using the on-the-fly probability enhanced sampling (OPES) method [74] with eight walkers sharing a common time-dependent bias and a BARRIER of 20 kcal mol⁻¹. Each walker was simulated for 12 ns, giving a total trajectory time of 96 ns per simulation. For uncertainty estimation, the 12-ns production period was partitioned into three consecutive 4-ns time blocks. Within each block, data from all eight walkers were combined and reweighted to obtain one block-specific PMF. The reported PMF is the mean of the three block-specific estimates, and the shaded bands represent two-sided 95% Student’s *t* confidence intervals calculated from these estimates. The 4-ns block length was selected based on convergence of the block-specific PMFs and to reduce temporal correlation between successive block estimates. The instantaneous Willard-Chandler interface [201] was calculated using the DISTANCE_FROM_CONTOUR implementation within

PLUMED. [88] PLUMED was also used to reweight the collective variables (CVs) to obtain the PMFs as a function of either the static or instantaneous surface. The results presented in Figures 2.1–2.4 were obtained with respect to the mean (static) Gibbs dividing surface (GDS).

2.5 Acknowledgements

Chapter 2, in full, has been accepted for publication in *Nature Communications*: **Henry Agnew**, Richa Rashmi, Xuanyu Zhu, Saswata Dasgupta, and Francesco Paesani, “Many-Body Interactions Resolve Halide Distribution at the Air/Water Interface,” *Nat. Commun.*, In Press. <https://doi.org/10.1038/s41467-026-77205-9> . The dissertation author was the primary investigator and author of this paper.

Chapter 3

Many-Body Ion–Ion Interactions

This chapter contains unpublished research that forms part of an ongoing effort to develop many-body potentials for alkali-metal–halide interactions in aqueous solution. Although the broader project is ongoing, the results and analyses reported here represent the completed scope of work included in this dissertation. Xuanyu Zhu and Marc Riera Rimbau were key collaborators in developing the potentials and interpreting the complex many-body interactions presented in this chapter.

3.1 Introduction

Ion–ion interactions are fundamental to modeling realistic aqueous solutions beyond the infinite-dilution limit. As the concentration increases, cation–anion encounters produce overlapping hydration environments and ion–ion correlations that are absent from single-ion systems. These collective interactions increasingly influence nonideal solution thermodynamics and, near saturation, the ionic chemical potentials that determine the solubility limit. [21] Ion pairing therefore provides a direct test of whether models developed for isolated-ion hydration remain transferable to concentrated solutions.

The association of oppositely charged ions in water is governed by a competition between

direct ion–ion attraction, ion hydration, and the reorganization of the surrounding hydrogen-bond network. As a cation and anion approach one another, the solvent structure changes from two largely independent hydration environments to configurations in which water molecules are shared or displaced. For aqueous NaCl, the two principal states considered here are the contact ion pair (CIP), in which Na^+ and Cl^- are in direct contact, and the solvent-shared ion pair (SSIP), in which at least one water molecule separates the ions. These states appear as distinct minima on the ion-pair free-energy profile and are separated by a solvent-reorganization barrier. [206, 134]

Accurately modeling this association requires a consistent balance among water–water, ion–water, and ion–ion interactions. Because each contribution changes as the ions approach and the solvent reorganizes, even modest errors in one component can alter the relative stability of the ion-pair states or the barrier between them. This sensitivity helps explain why empirical models optimized for a limited set of bulk observables can yield different ion-pair free-energy profiles. [38, 25, 134]

The relative thermodynamic stability of these configurations can be probed using the potential of mean force (PMF) as a function of the Na–Cl separation. The locations and depths of the PMF minima characterize the preferred ion-pair configurations, while the intervening barriers reflect the free-energy cost of reorganizing the solvent as the ions associate or dissociate. Because transitions between these basins may be rare on the timescale of an unbiased trajectory, umbrella sampling can be used to restrain the Na–Cl distance in a series of overlapping windows and reconstruct the corresponding free-energy profile. [191]

Although the Na–Cl separation provides a convenient reaction coordinate, it projects over solvent degrees of freedom such as water coordination and the formation of bridging-water configurations. The one-dimensional PMF must therefore be interpreted together with changes in the surrounding solvent structure.

The success of many-body potential energy functions depends in part on the rapid decay of short-range many-body contributions with increasing separation and body order. In models such as MB-pol, these short-range contributions are represented explicitly at low body orders,

while longer-range electrostatics and polarization are treated separately. [6,7,105,210] Although polarization represents an important component of the nonpairwise response, it does not by itself describe all short-range effects associated with overlap of the monomer electron densities, including Pauli repulsion, charge penetration, and charge transfer. [38, 163, 10] This physical separation is closely related to the “nearsightedness of electronic matter,” [149] through which the local electronic environment can often be understood without treating the entire system at the same level of detail. The difficulties encountered when extending this framework to ion–ion interactions, however, require us to revisit how rapidly the relevant many-body contributions converge. In particular, long-range Coulombic interactions remain important even when the ions are separated by several solvent molecules.

“It is generally accepted that, **in the absence of long-range ionic interactions**, large molecules or materials systems can be studied and understood one neighborhood at a time, without the necessity of studying the entire system at once.”

— Emil Prodan and Walter Kohn [149] (emphasis added)

For an isolated ion, the surrounding water molecules form an approximately radial hydration environment. Previous MB-nrg studies have shown that an explicit many-body description can accurately represent the hydration of individual alkali-metal cations and halide anions from finite clusters to bulk solution. [212, 36, 37] The simultaneous presence of a cation and an anion presents a more stringent test because it breaks the symmetry of the single-ion environment and produces a strongly directional electric field whose magnitude and orientation vary with the ion–ion separation. Water molecules located between the ions must respond to both ionic fields while maintaining favorable water–water hydrogen bonding. Consequently, mixed many-body contributions involving both ions and one or more water molecules may persist to higher body orders than water-only or single-ion contributions, particularly in configurations containing bridging water molecules.

Machine-learned interatomic potentials (MLIPs) provide an alternative route for representing high-dimensional potential energy surfaces, but their treatment of aqueous ion pairing depends strongly on the underlying architecture. Models based primarily on local atomic environments and finite cutoffs may not recover the long-range ion–ion interaction when the ions are connected neither directly nor through message-passing paths involving intervening atoms. [17,204] Models that augment a local representation with explicit electrostatics or polarization are designed to address this limitation, although they must still describe the short-range ion–ion–water interactions accurately. [16,132] Foundation MLIPs generally require large training sets containing cluster or bulk configurations, making less expensive electronic-structure methods such as ω B97M-V more practical than CCSD(T) for generating reference data. Consequently, their predictive accuracy depends on both the model architecture and the fidelity of the reference electronic-structure method.

Together, these considerations raise the central question addressed in this chapter: Are long-range electrostatics and polarization sufficient to describe aqueous ion pairing, or are explicit mixed ion–ion–water interactions required at higher body orders?

To examine these issues, we first use high-level electronic-structure calculations to characterize the many-body convergence of finite Na–Cl–water clusters. We then benchmark conventional force fields and several MLIPs on these cluster configurations against DLPNO-CCSD(T) and ω B97M-V reference energies, respectively, with particular attention to their behavior as the Na–Cl distance increases. Finally, we construct ion–ion–water many-body potentials of increasing body order and assess how their explicit many-body terms and polarization treatment influence the ion-pair PMF.

3.2 Methods

3.2.1 Cluster data set and electronic-structure calculations

The cluster benchmark set contained 180 configurations: ten cluster sizes, each with one Na^+ ion, one Cl^- ion, and an even number of water molecules from 0 through 18, evaluated at 18 Na–Cl separations. The separations were sampled at 0.25 Å intervals from 2.25 to 3.00 Å and at 0.50 Å intervals from 3.50 to 10.00 Å. The configurations spanned the contact, solvent-shared, and near-dissociation regions of the Na–Cl separation. All reference and model energies were evaluated on identical cluster geometries so that the comparisons isolate differences among the potential energy functions rather than differences caused by geometry optimization. Initial configurations were generated using PACKMOL [103] with the ions at prescribed separations, after which the water coordinates were optimized with the JC/TIP4P-Ew model. Representative Na–Cl–3H₂O configurations are shown in Figure 3.2.

DLPNO-CCSD(T) and ω B97M-V single-point calculations were performed with ORCA 6.0. [119, 122, 194, 69, 94, 120, 125, 63, 121, 123, 124, 166, 168, 167, 22] The NaCl–water clusters were treated as neutral singlets. The DLPNO-CCSD(T) calculations used the TightPNO thresholds, TightSCF convergence, and a frozen-core approximation based on ORCA’s FC_ELECTRONS definition. The primary basis was cc-pwCVTZ for Na and aug-cc-pVTZ for all other atoms. The Coulomb-fitting auxiliary basis was generated with AutoAux for Na and was aug-cc-pVTZ/C for the remaining atoms; the auxiliary space was handled using PCDTrimAuxC Coulomb and PCDThresh -1. Each calculation used eight parallel processes, with MaxCore set to 6000 MB per process and the maximum number of SCF iterations set to 300.

The ω B97M-V calculations used the def2-TZVPPD basis set for all atoms, the SCNL and TightSCF options, the DEFGRID3 integration grid, and the RIJCOSX approximation with the def2/J auxiliary basis. Each calculation used 16 parallel processes, with MaxCore set to

4000 MB per process and the maximum number of SCF iterations set to 1000.

For each cluster size and electronic-structure method, the resulting energy profile was referenced to its value at a Na–Cl separation of 10 Å.

3.2.2 Many-body decomposition

The full many-body decomposition was performed for a Na–Cl–10H₂O cluster with a Na–Cl separation of 2.75 Å. This cluster was extracted from a JC/TIP4P-Ew trajectory of bulk NaCl solution to represent the contact ion pair state.

Treating the two ions and each water molecule as separate monomers gives a 12-monomer system whose energy can be written as

$$E_N(1, \dots, N) = \sum_{n=1}^N \sum_{1 \leq i_1 < \dots < i_n \leq N} \Delta E^{(n)}(i_1, \dots, i_n), \quad (3.1)$$

where $\Delta E^{(n)}$ is the nonadditive contribution associated with a particular n -monomer subset after all lower-order contributions have been removed. All terms through the 12B contribution were evaluated. The subclusters were partitioned into four categories: water-only subsets, subsets containing Na⁺ but not Cl[−], subsets containing Cl[−] but not Na⁺, and subsets containing both ions. This partitioning separates the convergence of water-only and single-ion contributions from that of mixed contributions involving both ions.

The subcluster energies entering the decomposition were counterpoise corrected in ORCA to reduce basis-set superposition error. [26] The same DLPNO-CCSD(T) basis-set combination described above was used for every term in the decomposition. In each subcluster calculation, the constituent monomers retained the geometries and relative coordinates they had in the full Na–Cl–10H₂O cluster.

3.2.3 Force-field and machine-learned-potential benchmarks

The force-field comparison included the nonpolarizable JC/TIP4P-Ew [82, 67] and Madrid-2019 [208, 24] models, the polarizable iAMOEBA model, [148] and a preliminary MB-nrg model containing an explicit 2B Na-Cl term. Their energies were compared with the DLPNO-CCSD(T) reference values on the cluster benchmark set. The MLIP comparison included UMA, MACE-OMOL, MACE-POLAR-1, and OrbMol-v2. [204, 17, 16, 132] Because these molecular foundation models were trained using ω B97M-V data, their cluster energies were compared with the ω B97M-V reference values.

For both benchmarks, the plotted residual was defined as $\Delta E_{\text{res}} = E_{\text{model}} - E_{\text{reference}}$. Thus, a positive residual indicates that the model energy is too high relative to the reference, whereas a negative residual indicates that it is too low. Chemical accuracy was defined here as $|\Delta E_{\text{res}}| \leq 1 \text{ kcal mol}^{-1}$.

The JC/TIP4P-Ew and Madrid-2019/TIP4P/2005 energies were evaluated with the 10 December 2025 version of LAMMPS (commit be4579548a). The iAMOEBA energies were evaluated with Tinker 7.1.2 using the `iamoeba-nacl.prm` parameter file. All cluster calculations were nonperiodic and used a 100 Å direct-space cutoff without Ewald summation or particle-mesh Ewald (PME); direct polarization was used for iAMOEBA.

All MLIP calculations were performed on nonperiodic, neutral-singlet clusters. UMA calculations used the `uma-m-1p1` model in `fairchem-core 2.21.0` with the default `float32` inference settings. MACE 0.3.17 calculations used the `extra_large` MACE-OMOL-0 model and the MACE-POLAR-1-M model in `float64` precision. Both UMA-M-1.1 and MACE-OMOL-0 use a 6 Å radial neighbor cutoff. UMA-M-1.1 contains ten message-passing blocks, whereas MACE-OMOL-0 contains three interaction blocks, giving maximum multi-hop graph-path lengths of 60 and 18 Å, respectively; reaching those distances requires chains of intervening atoms. [204, 17] MACE-POLAR-1-M used its built-in long-range electrostatics with no external electric field. OrbMol-v2 calculations used `orb-models 0.7.0` with `float32-highest` precision;

its built-in all-pairs Coulomb contribution was included.

3.2.4 Construction of the many-body potentials

The ion-pair models were constructed within the MB-nrg framework by combining MB-pol water–water interactions with existing Na^+ –water and Cl^- –water interactions and newly fitted Na–Cl, Na–Cl–water, and Na–Cl–water–water terms. [6, 7, 212, 36] Here, IW, IWW, II, IIW, and IIWW denote ion–water, ion–water–water, ion–ion, ion–ion–water, and ion–ion–water–water interactions, respectively. Four nested interaction hierarchies were examined: (1) IW and II; (2) IW, IWW, and II; (3) IW, IWW, II, and IIW; and (4) IW, IWW, II, IIW, and IIWW. Long-range electrostatics and induction were treated by the underlying electrostatic and polarization terms of MB-nrg, while the new IIW and IIWW terms describe short-range nonadditive interactions explicitly.

The short-range II, IIW, and IIWW terms were fitted to counterpoise-corrected CCSD(T) interaction energies calculated with MOLPRO 2019.2. [198, 199] The basis combination depended on body order: cc-pwCV5Z for Na and aug-cc-pV5Z for all other atoms at the 2B level; cc-pwCVQZ and aug-cc-pVQZ at the 3B level; and cc-pwCVTZ and aug-cc-pVTZ at the 4B level. The counterpoise correction was applied to reduce basis-set superposition error (BSSE).

The IIW Na–Cl– H_2O term was represented by a fifth-degree polynomial, whereas the IIWW Na–Cl– $(\text{H}_2\text{O})_2$ term used a fourth-degree polynomial. Both terms used a fitting cutoff of 7.5 Å.

To assess the coupling between explicit short-range terms and many-body induction, three fixed chloride polarizability settings were tested: pol100 (5.3602 Å^3), poleff (2.6569 Å^3), and pol0 (0 Å^3). The effective polarizability used for poleff was obtained using the exchange-hole dipole moment (XDM) method following the procedure described by Caruso et al. [37].

3.2.5 Potential-of-mean-force calculations

Molecular dynamics simulations of the many-body models were performed using the 22 July 2025 Update 2 version of LAMMPS [189] coupled to MBX v1.3 [162,59] and PLUMED. [192] Each system contained one $\text{Na}^+ - \text{Cl}^-$ pair and 277 flexible water molecules, for a total of 833 atoms and an NaCl concentration of approximately 0.20 mol L^{-1} . The simulations used a periodic cubic cell with a mean side length of approximately $20.21 \text{ \AA}$ and were performed in the isotropic isothermal–isobaric ensemble at 298 K and 1 atm. The equations of motion were integrated with a 0.5 fs time step. Nosé–Hoover thermostat and barostat damping times of 50 and 500 fs, respectively, were used. The water molecules were fully flexible, with no SHAKE or RATTLE constraints.

The 2B and 3B cutoff distances were 9.0 and $7.5 \text{ \AA}$, respectively. Long-range electrostatics and dispersion were treated using PME with an Ewald splitting parameter of $0.60 \text{ \AA}^{-1}$, a reciprocal-space grid density of 2.5, and sixth-order interpolation. The induced dipoles were converged by conjugate gradients to a tolerance of 10^{-8} , with a maximum of 100 iterations.

The Na–Cl separation, R_{NaCl} , was sampled using umbrella sampling with a harmonic bias in window i ,

$$U_i^{\text{bias}}(R_{\text{NaCl}}) = \frac{1}{2}k_i (R_{\text{NaCl}} - R_i)^2, \quad (3.2)$$

where R_i is the center of the window and k_i is the corresponding restraint strength. A total of 32 windows spanning $2.25\text{--}10.00 \text{ \AA}$ were sampled at $0.25 \text{ \AA}$ intervals using $k_i = 25 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$. Each window was equilibrated for 200 ps and sampled for an additional 200 ps. The Na–Cl distance was recorded every 0.1 ps.

The biased distance distributions were combined using the Grossfield implementation of the one-dimensional weighted histogram analysis method (WHAM) to reconstruct the PMF at 298 K. [191, 91] The interval from 2 to $10 \text{ \AA}$ was divided into 100 bins of width $0.08 \text{ \AA}$, and WHAM was converged to a tolerance of 10^{-8} . A radial Jacobian correction of $2k_{\text{B}}T \ln R_{\text{NaCl}}$ was added to the reconstructed PMF, which was then referenced to zero at the center of the

largest-distance bin, $R_{\text{NaCl}} = 9.96 \text{ \AA}$.

Statistical uncertainties were estimated by dividing each 200 ps production trajectory into four nonoverlapping 50 ps blocks and repeating the WHAM analysis for each block. The reported intervals are two-sided 95% Student’s t confidence intervals calculated from the four block PMFs. Histogram overlap between neighboring umbrella windows was inspected as an additional qualitative convergence check.

3.3 Results

3.3.1 Many-body convergence of Na–Cl–H₂O clusters

To examine the prevalence of many-body interactions for these aqueous alkali-metal halide systems, we first performed a full many-body decomposition of a cluster and partitioned the many-body contributions based on the influence of the ions. Figure 3.1 reports the full many-body decomposition of a Na–Cl–10H₂O cluster using DLPNO-CCSD(T) with counterpoise correction. An untruncated version of this figure that goes up to 12B is included in the Appendix as Figure A.2. The Na–Cl distance of 2.75 $\text{\AA}$ used for this decomposition represents the short-range CIP configuration, in which the two ions are directly exposed to each other.

In Figure 3.1(A), the many-body contributions for subclusters containing only water decay quickly and are negligible above the 3B level. This behavior is consistent with the explicit short-range representation in MB-pol, which includes water–water 2B [6] and 3B [7] terms. The Na–water and Cl–water categories exhibit clear 2B and 3B contributions, with a weaker 4B signature. This behavior broadly aligns with existing MB-nrg ion–water models that include explicit terms through 3B. [212, 36]

In contrast, the mixed-ion category exhibits substantial higher-body contributions through 5B and a smaller but non-negligible 6B contribution. In this cluster, the summed mixed-ion contribution is 5.3 kcal mol^{−1} at 5B and −1.4 kcal mol^{−1} at 6B, and it becomes

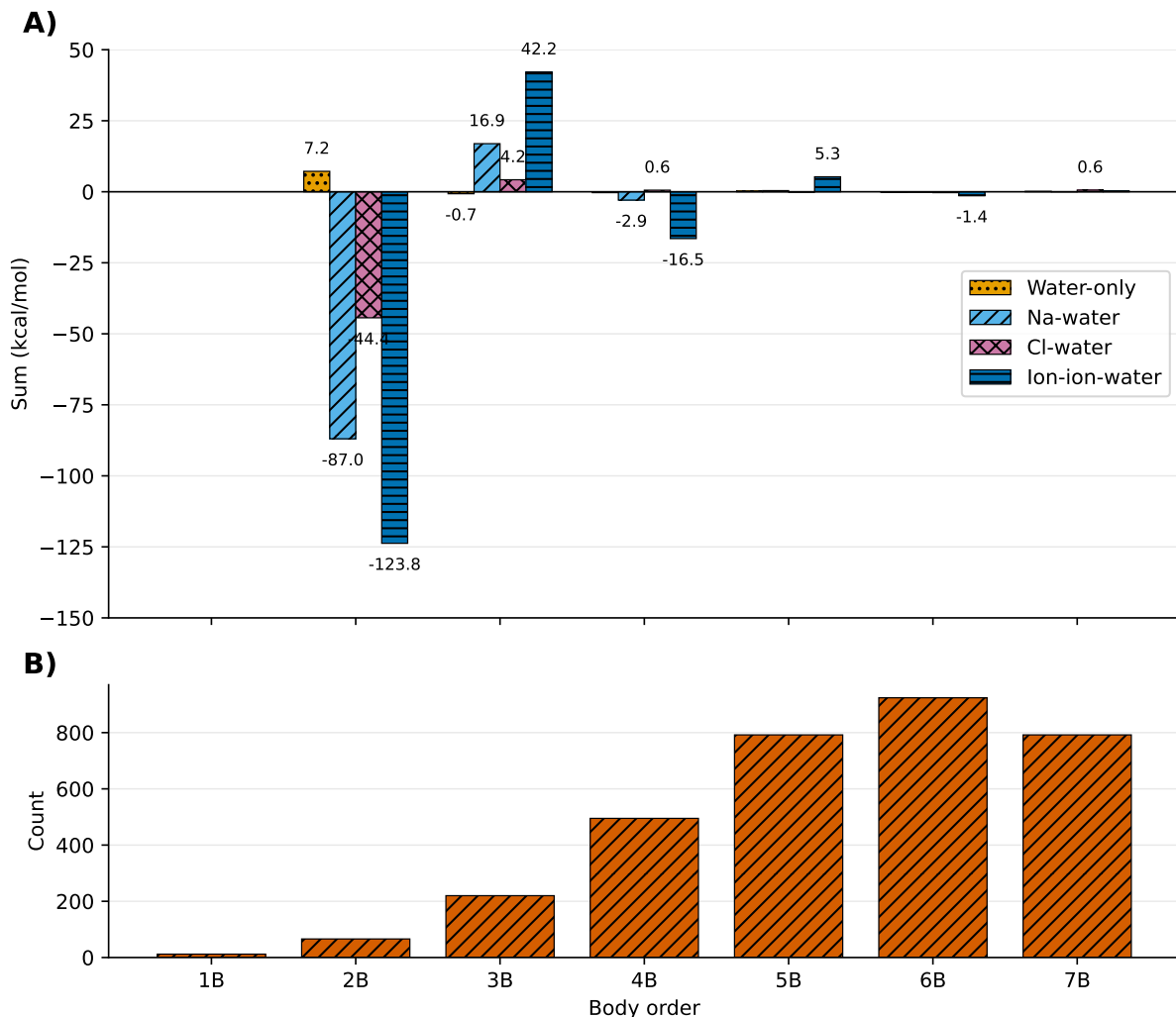


Figure 3.1: Many-body decomposition of a Na–Cl cluster with 10 surrounding water molecules. The ions are separated by a distance of 2.75 Å. (A) Sums of the many-body contributions partitioned into water-only subclusters, subclusters containing Na but not Cl, subclusters containing Cl but not Na, and subclusters containing both ions. (B) Total number of terms at each body order, illustrating the combinatorics of the decomposition.

negligible by 7B. The strong, directional electric field between the ions makes the intervening water molecules particularly sensitive to many-body polarization and short-range quantum-mechanical effects.

In Figure 3.1(B), the body-order histogram highlights the importance of the combinatorial amplification of many-body interactions as the system size increases. Although higher-body terms generally decrease in magnitude with increasing body order, the number of distinct n -

body combinations grows rapidly with the number of monomers. Consequently, the cumulative contribution may remain significant even when the individual terms are small. This effect can become increasingly important when extrapolating from finite clusters to the bulk limit, where the number of possible combinations at a given body order n grows as $\binom{N}{n}$. This counting argument alone does not establish the magnitude of the bulk contribution, however, because spatial locality, electrostatic screening, and cancellation among terms can substantially reduce the net effect.

Taken together, these results indicate that truncation schemes developed for neat water or isolated ion–water systems may not transfer directly to solutions containing both cations and anions. The persistence of mixed-ion contributions through higher body orders, combined with the combinatorial growth in the number of such contributions, suggests that accurate models of concentrated and bulk electrolyte solutions may require higher-order ion–ion–water effects to be represented either explicitly or through an effective many-body treatment.

3.3.2 Comparison to current machine-learned potentials and force fields

Given that higher-body effects are prominent for these clusters, it is worth investigating how they depend on the ion–ion distance and influence ion desolvation during pairing.

Figure 3.2 shows representative Na–Cl–3H₂O clusters in the (A) CIP, (B) SSIP, and (C) near-dissociation regions. These optimized gas-phase clusters illustrate how the water molecules reorganize in response to competing ion–ion, ion–water, and water–water interactions, although they do not reproduce the full solvent environment of the bulk solution.

In the CIP configuration, the ions are in direct contact and the confined water molecules cannot simultaneously adopt their preferred orientations relative to both ions and to one another. The resulting geometry reflects competition among ion–water interactions, water–water hydrogen bonding, and steric constraints. Although this pentamer is not the Na–Cl–10H₂O cluster used for the decomposition in Figure 3.1, it illustrates the type of bridging-water motif that can

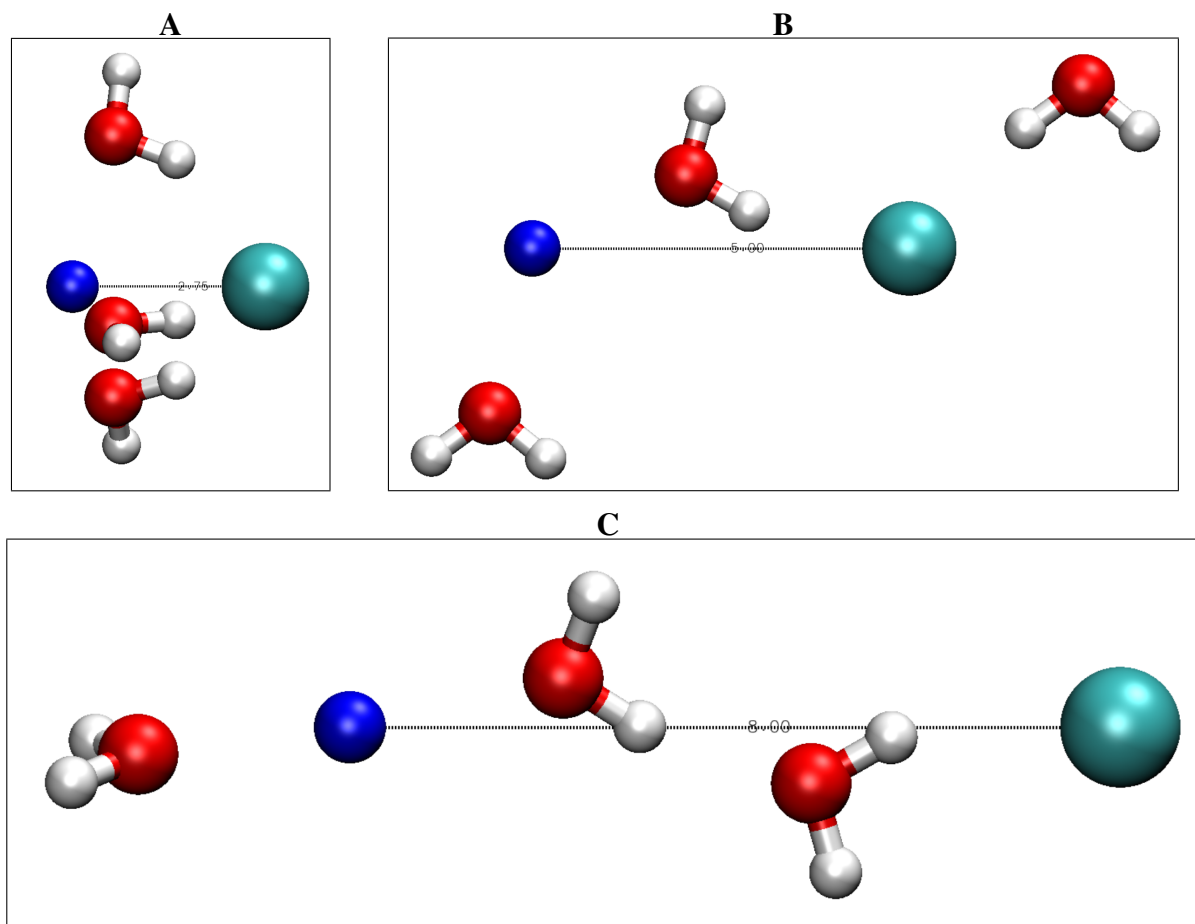


Figure 3.2: Representative Na–Cl–3H₂O cluster configurations at Na–Cl separations of (A) 2.75 Å (CIP), (B) 5.00 Å (SSIP), and (C) 8.00 Å (near-dissociation). Clusters were optimized with JC/TIP4P-Ew.

generate mixed higher-body couplings.

In the SSIP configuration, the larger ion–ion separation allows a water molecule to bridge the ions with a more favorable orientation of its hydrogen atoms and lone pairs. At the near-dissociation separation in Figure 3.2(C), multiple solvent layers begin to form. Hydrogen bonding persists among the waters between the ions, indicating that the two hydration environments are not yet fully independent.

Figure 3.3 compares the energies predicted by selected force fields with DLPNO-CCSD(T) reference energies of Na–Cl clusters containing up to 18 water molecules. Panels (A) and (B) show results for the nonpolarizable, pairwise Joung and Cheatham (JC) [82] and

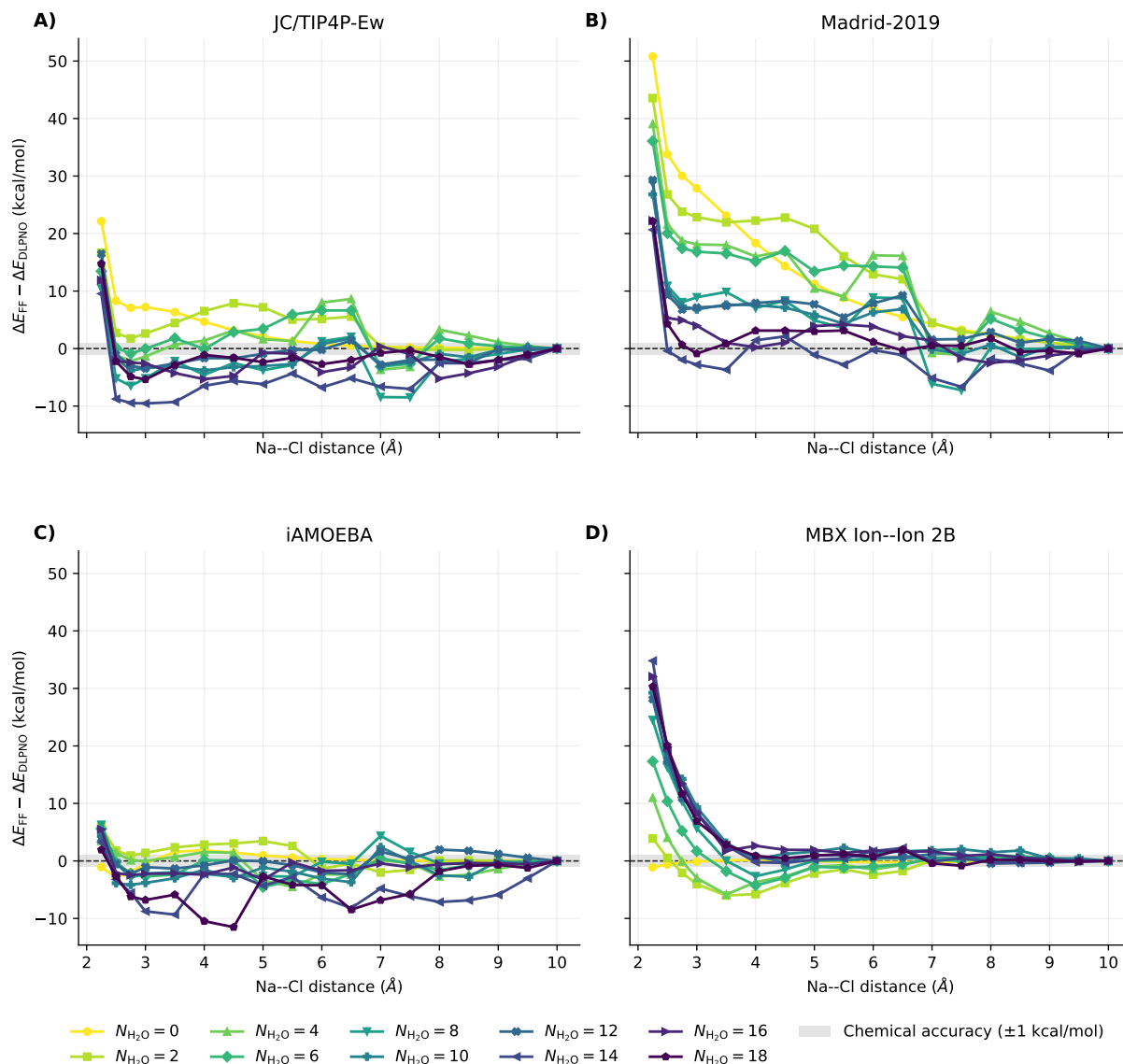


Figure 3.3: Force-field residuals of Na-Cl-H₂O clusters compared with a DLPNO-CCSD(T) reference. Force fields include the nonpolarizable (A) JC/TIP4P-Ew and (B) Madrid-2019 potentials, the polarizable (C) iAMOEBA potential, and (D) a prototypical MB-nrg potential with only 2B ion-ion interactions. The ten series represent clusters containing 0, 2, ..., 18 water molecules. The shaded horizontal band denotes chemical accuracy, $|\Delta E_{\text{res}}| \leq 1$ kcal mol⁻¹.

Madrid-2019 [208, 24] potentials, respectively. These potentials are empirically parameterized to incorporate polarization effects implicitly and reproduce bulk properties. The JC residuals depend strongly on both hydration and ion separation: the bare ion pair is too high in energy at short range, while several hydrated clusters are too low in energy by nearly 10 kcal mol⁻¹

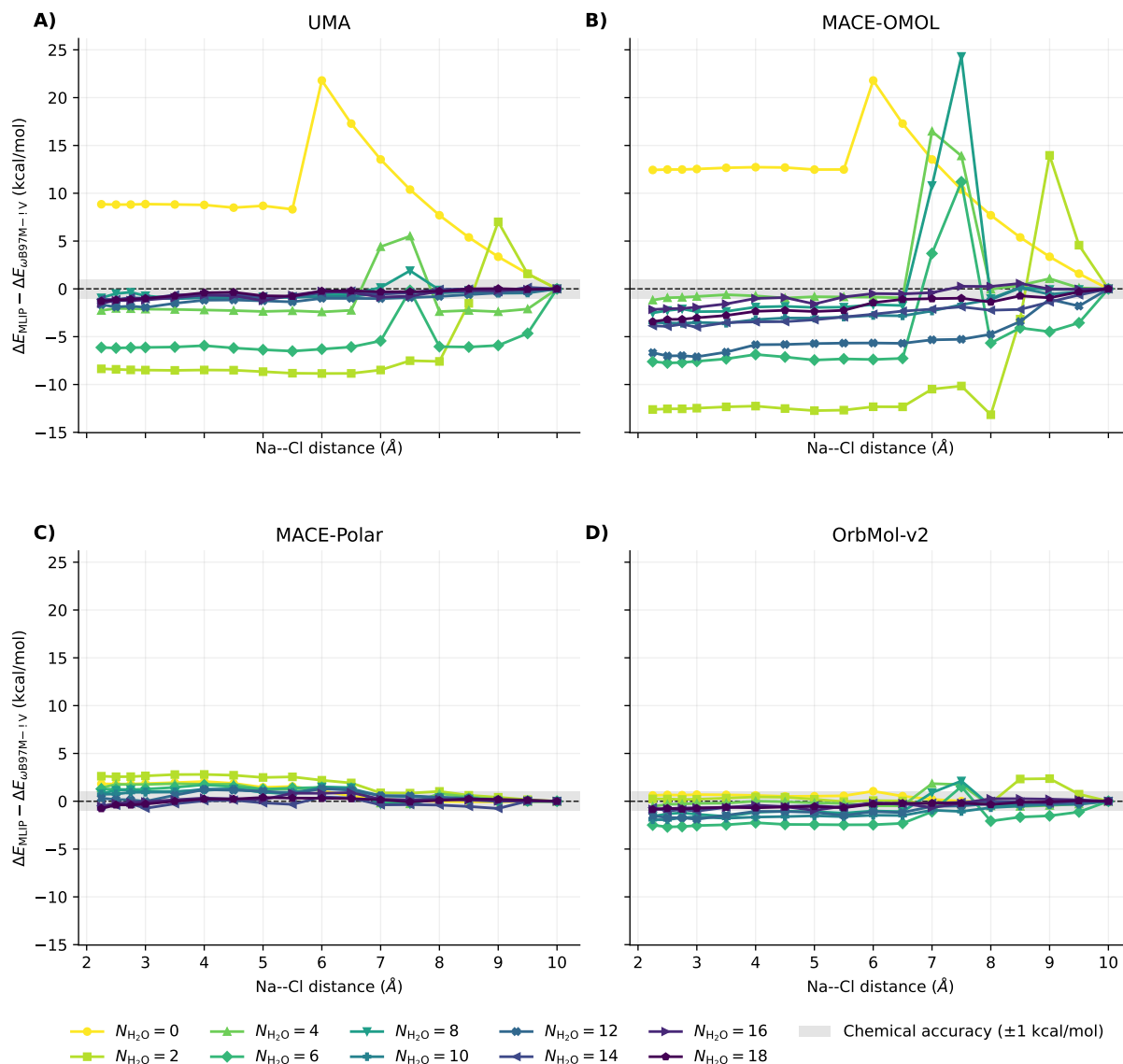


Figure 3.4: MLIP residuals of Na-Cl-H₂O clusters compared with an $\omega\text{B97M-V}$ reference. MLIPs include (A) UMA, (B) MACE-OMOL, (C) MACE-POLAR-1, and (D) OrbMol-v2. The ten series represent clusters containing 0, 2, ..., 18 water molecules. The shaded horizontal band denotes chemical accuracy, $|\Delta E_{\text{res}}| \leq 1 \text{ kcal mol}^{-1}$.

across parts of the sampled range. In contrast, Madrid-2019 is predominantly too high in energy and produces the largest positive residuals, particularly for the smaller clusters and shortest separations. Madrid-2019 uses scaled ionic charges of $\pm 0.85e$ and was parameterized primarily against bulk properties. The reduction in its residual for some larger clusters is consistent with this bulk-focused parameterization, although it does not by itself establish convergence to the

bulk limit. Figure 3.3(C) shows results for the polarizable iAMOEBA potential. Because this model includes explicit polarization, it describes the unshielded interaction of the bare ion pair more accurately than the two nonpolarizable models. Its residuals nevertheless frequently lie outside chemical accuracy. Several highly hydrated clusters are too low in energy across intermediate separations, while positive errors remain at the shortest separation for multiple cluster sizes. The resulting pattern indicates that the deficiencies are not confined to the bare ion pair or to the shortest-range interaction. Figure 3.3(D) shows results for an MB-nrg potential with explicit 2B ion–ion interactions, the existing ion–water terms, and MB-pol water–water interactions. Its ion–ion interactions are not parameterized empirically but are instead fitted to CCSD(T) dimer energies. This potential captures the bare ion–ion interaction well, but the large positive residuals for hydrated clusters at the shortest separation and negative residuals across parts of the CIP and SSIP regions demonstrate the need for higher-body corrections. These corrections must provide configuration-dependent attraction at the shortest separations and repulsion at larger separations. For $R_{\text{NaCl}} > 5 \text{ \AA}$, its residuals vary smoothly with separation and are more tightly grouped than those of the other force-field models, indicating better-behaved intermediate- to long-range energetics despite the remaining short-range deficiencies.

As an additional comparison, we examine how machine-learned potentials perform on the same clusters. Architectures built primarily from local atomic environments can have difficulty representing strong, long-range electrostatic interactions.

Figure 3.4 illustrates the errors of several machine-learned interatomic potentials relative to an ω B97M-V reference, consistent with the electronic-structure level used to train these models. This figure compares UMA, MACE-OMOL, MACE-POLAR-1, and OrbMol-v2. UMA [Figure 3.4(A)] [204] and MACE-OMOL [Figure 3.4(B)] [17] exhibit substantial cluster-size-dependent offsets across much of the sampled range, together with abrupt deviations at intermediate-to-long Na–Cl separations. For the bare ion pair, the Na and Cl atoms cease to share a direct graph edge beyond the common $6 \text{ \AA}$ cutoff. In the hydrated clusters, water-mediated paths can transmit information over longer distances, up to the maximum multi-hop ranges

given above. The shifting locations of the deviations with cluster size are therefore consistent with a dependence on the available local message-passing paths, although the present data do not establish that the cutoff alone causes each feature. MACE-POLAR-1 [Figure 3.4(C)] [16] and OrbMol-v2 [159, 132] [Figure 3.4(D)] instead contain explicit electrostatic terms and do not exhibit the same pronounced deviations. Their residuals remain substantially smaller than those of UMA and MACE-OMOL, but neither model remains within chemical accuracy for every cluster and separation. MACE-POLAR-1 is generally too high in energy for the smaller clusters and the bare ion pair, whereas OrbMol-v2 is modestly too low in energy for several hydrated clusters. The ω B97M-V reference itself also retains functional-driven errors relative to CCSD(T), as shown in Appendix Figure A.3. Taken together, these results demonstrate that an accurate description of aqueous ion pairing requires more than a representation of local atomic environments. The systematic offsets and intermediate-to-long-range deviations of MACE-OMOL and UMA highlight the importance of recovering ion–ion behavior even for these smaller clusters. At the same time, the remaining errors indicate the difficulty of accurately capturing the shorter-range interactions of the intervening water molecules. These observations motivate a physically structured approach that combines explicit long-range electrostatics and polarization with short-range ion–ion–water many-body terms. In the following section, we examine the construction of such many-body potentials and assess their influence on the ion-pair potential of mean force.

3.3.3 Constructing many-body potentials

Building upon the MB-pol potential for water and our existing ion–ion NaCl potential, we add explicit higher-body effects and examine their influence on the potential of mean force. We also vary the polarizability to diagnose the implicit many-body effects of the polarization term.

Figure 3.5 contains potentials of mean force with increasing sets of explicit many-body

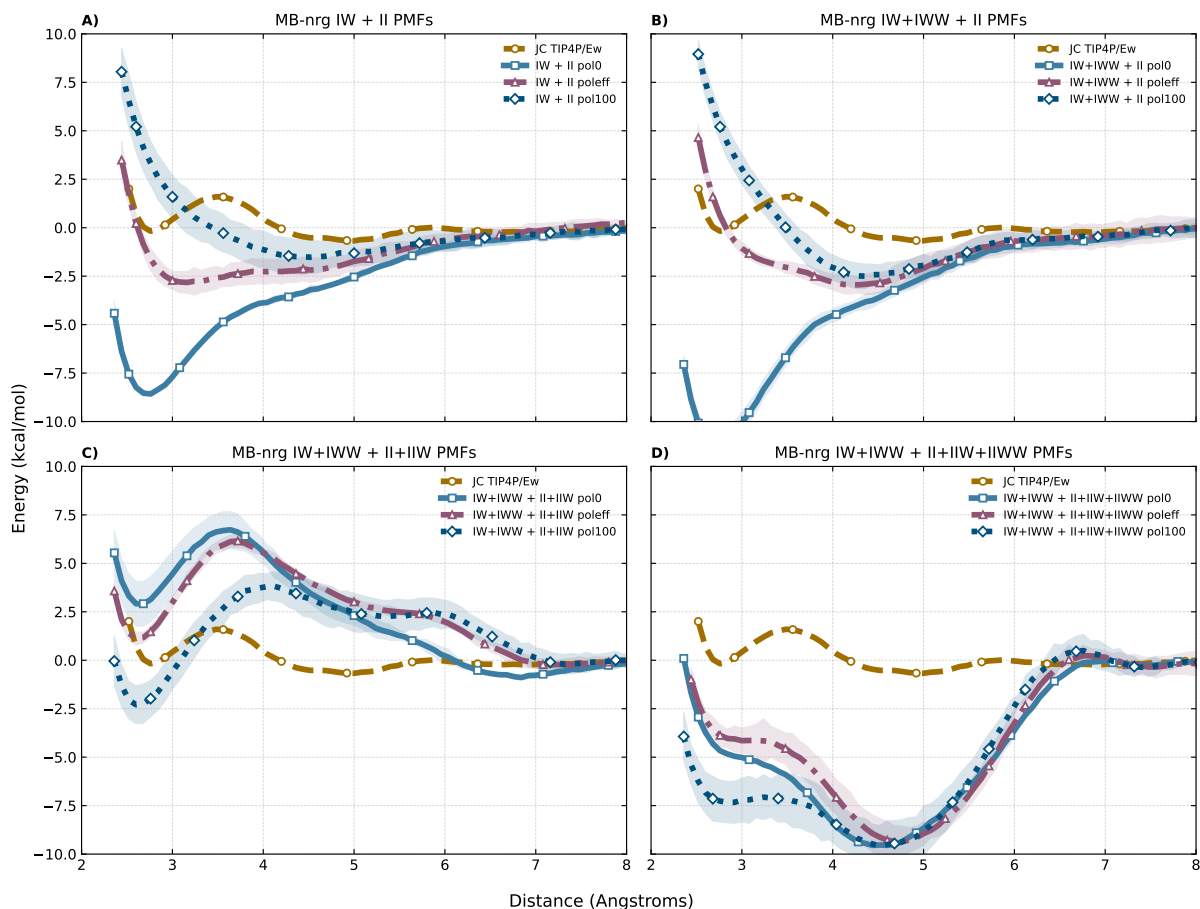


Figure 3.5: Potentials of mean force combining MB-pol with (A) ion–water and ion–ion, (B) ion–water, ion–water–water, and ion–ion, (C) ion–water, ion–water–water, ion–ion, and ion–ion–water, and (D) ion–water, ion–water–water, ion–ion, ion–ion–water, and ion–ion–water–water interactions. Here, IW, IWW, II, IIW, and IIWW denote ion–water, ion–water–water, ion–ion, ion–ion–water, and ion–ion–water–water interactions, respectively. The dashed line gives the JC/TIP4P-Ew model PMF, which provides a qualitative guide to the expected positions of the CIP and SSIP wells. Shaded bands are two-sided 95% Student’s t confidence intervals calculated from the four block PMFs. Some strongly attractive curves in panels (B) and (D) extend below the plotted lower limit of $-10 \text{ kcal mol}^{-1}$.

terms. All of these PMFs use MB-pol for the water–water interactions. We tested different fixed polarizabilities to investigate the effects of implicit many-body polarization on the explicit many-body terms and resulting PMF. Panels (A) and (B) model the ion–ion interaction explicitly only through a 2B term. The PMF with full gas-phase polarizability (pol100, $5.3602 \text{ \AA}^3$) produces an SSIP well but does not exhibit a CIP minimum. In contrast, the effective polarizability

(poleff, $2.6569 \text{ \AA}^3$) and zero polarizability (pol0, $0 \text{ \AA}^3$) produce a CIP well. The addition of ion–water–water interactions in Figure 3.5(B) causes only modest changes to the well depths. A central shortcoming of these PMFs is that each has only one distinct minimum rather than the expected two-minimum CIP/SSIP structure. [206, 134]

In Figure 3.5(C), the addition of 3B ion–ion–water terms substantially alters the PMFs. All three polarizability settings resolve a CIP minimum, but the profiles become much more repulsive than the JC/TIP4P-Ew guide in the expected SSIP region between 4 and 5 $\text{\AA}$. Figure 3.5(D) adds explicit ion–ion–water–water interactions. The pol100 and poleff models exhibit features associated with both the CIP and SSIP, but they substantially over-stabilize the ion pair relative to the JC/TIP4P-Ew profile. Portions of these strongly attractive PMFs fall below the plotted lower limit, emphasizing that the current models are not yet quantitatively reliable.

The oscillatory behavior in this figure is reminiscent of that in Figure 3.1: the 3B ion–ion–water contribution is repulsive, whereas the 4B ion–ion–water–water contribution is attractive for the decomposed cluster. The 5B behavior in Figure 3.1 suggests that an explicit 5B contribution may be repulsive for similar configurations, although this sign need not transfer across all configurations sampled by the PMF.

Additionally, the large differences among the polarizability models suggest that the underlying electrostatic model may require refinement. Current MB-nrg models use fixed polarizabilities within the TTM4-F polarization framework. Although this approach has been successful for models such as MB-pol, the strong electrostatics in aqueous electrolyte solutions may require a more flexible treatment. One possibility is a variable polarizability that depends on the Na–Cl separation or on the local hydration environment. [62] Such a treatment could incorporate a larger fraction of the higher-body response through polarization and thereby reduce the magnitude required of explicit higher-body corrections.

3.4 Conclusions and Outlook

This chapter examined how the simultaneous presence of a cation and an anion changes the many-body interactions that must be represented to describe aqueous ion pairing. In the Na–Cl–10H₂O cluster considered here, water-only and single-ion contributions decay rapidly with body order, whereas mixed contributions containing both ions remain significant through 5B and retain a smaller contribution at 6B. Although a decomposition of one finite cluster cannot establish the convergence behavior of every bulk configuration, it demonstrates that truncation schemes developed for neat water or isolated ion hydration do not necessarily transfer directly to configurations in which cation and anion hydration environments overlap.

The cluster benchmarks further show that long-range ion–ion interactions pose a distinct challenge for both conventional force fields and machine-learned potentials. The empirical force fields exhibit systematic, model-dependent residuals across cluster size and ion–ion separation. Among the MLIPs, local architectures develop substantial cluster-size-dependent offsets and pronounced intermediate-to-long-range deviations, whereas models containing explicit electrostatic terms avoid the largest errors. The remaining errors of these electrostatic MLIPs, however, show that a long-range treatment alone does not guarantee an accurate description of the shorter-range interactions involving the intervening water molecules.

The successive MB-nrg models provide a direct illustration of this balance. Models containing only explicit 2B ion–ion interactions produce either a CIP or an SSIP minimum, but not the expected two-basin structure. Adding the 3B ion–ion–water term restores a CIP minimum while making the SSIP region excessively repulsive, and adding the 4B ion–ion–water–water term introduces features associated with both states but substantially over-stabilizes the ion pair. The strong dependence of these PMFs on the fixed chloride polarizability also indicates that the partitioning between explicit short-range terms and many-body polarization is not yet balanced. Taken together, these results answer the central question of this chapter: long-range electrostatics and polarization are essential but are not sufficient on their own. Mixed ion–ion–water effects

must also be captured, either through explicit higher-body terms or through an effective many-body representation.

The present MB-nrg potentials should therefore be viewed as diagnostic models rather than final potentials for aqueous electrolyte simulations. Future work should expand the training sets across the CIP, SSIP, and dissociation regions; refine the short-range fits and their switching behavior; and determine whether an environment-dependent polarization model can absorb part of the higher-body response without sacrificing accuracy or transferability. These developments should be evaluated against both high-level cluster benchmarks and statistically converged bulk PMFs over a broader range of concentrations and ion identities. Such tests will determine the most efficient division of the interaction energy between explicit short-range many-body terms and the underlying electrostatic and polarization model.

3.5 Acknowledgments

Chapter 3 contains unpublished, ongoing work on many-body ion–ion potentials. Marc Riera Riambau and Xuanyu Zhu were key collaborators in developing the potentials and interpreting the many-body ion–ion interactions presented here. The dissertation author was the primary investigator and author of this work.

Chapter 4

Conclusions and Outlook

4.1 Synthesis

The results presented in this dissertation demonstrate that the behavior of ions in water cannot be understood from ionic size, charge density, or polarizability alone. Instead, aqueous ion specificity emerges from a balance among long-range electrostatics, short-range quantum-mechanical interactions, many-body polarization, and the collective reorganization of the surrounding hydrogen-bond network. By examining this balance across bulk hydration, the air/water interface, and aqueous ion pairing, this work establishes many-body interactions not merely as corrections to pairwise models, but as essential contributions that determine molecular structure, dynamics, spectroscopy, and thermodynamics.

Chapter 1 established this connection for the hydration of individual halide ions. Fluoride differs qualitatively from the heavier halides because its small size and high charge density produce short, directional hydrogen bonds with neighboring water molecules. These interactions generate a well-defined hydration shell, slow water exchange, enhanced water polarization, and pronounced changes in the infrared spectrum. The particularly large red shift of the OH-stretching band cannot be explained by electrostatic polarization alone and instead reflects short-range effects associated with partial charge transfer along the $\text{F}^- \cdots \text{H}-\text{O}$ hydrogen bond.

Chloride, bromide, and iodide interact more weakly with water, and their structural and spectroscopic perturbations are largely confined to the first hydration shell. These trends show both the locality of isolated-ion hydration and the importance of an explicit many-body description when the local interaction becomes sufficiently strong and directional.

Chapter 2 then examined how these ion–water interactions change in an inhomogeneous environment. A controlled hierarchy of many-body models showed that pairwise-additive interactions exclude all four halides from the air/water interface, whereas classical polarization combined with conventional repulsion and dispersion over-stabilizes the heavier halides. The full MB-nrg description produces an intermediate result: fluoride, chloride, and bromide remain thermodynamically bulk-favored, while iodide exhibits only a shallow interfacial minimum of order $k_B T$. The many-body energy decomposition attributes this weak iodide preference to a favorable water cavity/reorganization contribution that offsets ion–water desolvation near the Gibbs dividing surface. An opposing entropic penalty prevents this energetic stabilization from producing a deep free-energy minimum. Halide surface propensity therefore emerges from a many-body balance between local ion–water interactions and collective solvent response rather than from ionic softness or polarizability alone.

Chapter 3 extended this framework beyond the isolated-ion limit to configurations in which cation and anion hydration environments overlap. The many-body decomposition of a Na–Cl–10H₂O cluster showed that mixed contributions involving both ions persist to higher body orders than the water-only and single-ion contributions. The cluster benchmarks further exposed complementary limitations of current modeling strategies: local machine-learned potentials develop substantial cluster-size-dependent offsets and pronounced intermediate-to-long-range deviations, while architectures containing explicit electrostatics avoid the largest errors but retain shorter-range residuals. Conventional force fields similarly exhibit systematic, model-dependent deviations from the electronic-structure references.

The preliminary MB-nrg ion-pair models clarify why neither long-range electrostatics nor additional short-range terms can be considered independently. Adding explicit ion–

ion–water and ion–ion–water–water interactions changes the qualitative shape of the Na–Cl potential of mean force, but the resulting profiles remain highly sensitive to the chloride polarizability. The current models either fail to resolve both the contact and solvent-shared ion-pair states or over-stabilize one portion of the free-energy profile. These results establish that long-range electrostatics and polarization are necessary but not sufficient for aqueous ion pairing. Mixed short-range interactions must also be represented, either explicitly at higher body orders or through an effective many-body treatment that preserves the correct coupling between the ions and their shared solvent environment.

Taken together, the three studies reveal a progression in many-body complexity. For an isolated ion in bulk water, the strongest ion-specific effects are predominantly local and decay rapidly outside the first hydration shell. At an interface, these local interactions compete with collective solvent reorganization and entropy. At finite concentration, overlapping ionic fields couple multiple hydration environments and can sustain mixed contributions to higher body orders. The appropriate many-body representation is therefore inseparable from the physical environment: a truncation that is accurate for an isolated ion may not remain transferable to an interface or an ion pair.

4.2 Outlook

The most immediate next step is to complete and validate the ion–ion many-body potentials. This will require broader training sets spanning contact, solvent-shared, and dissociated configurations; careful optimization of the higher-body polynomial and switching representations; and systematic assessment against both high-level cluster energies and converged bulk free-energy profiles. The strong sensitivity to the fixed chloride polarizability also motivates an environment-dependent polarization model that can respond to ion–ion separation and local hydration. Such a model may incorporate part of the higher-body response through induction and reduce the magnitude and complexity required of the explicit short-range corrections.

Completing the ion-pair description would also connect the latter two chapters of this dissertation. The interfacial calculations considered the dilute single-ion limit, whereas experimentally relevant electrolyte interfaces contain both cations and anions and exhibit concentration-dependent ion-ion correlations. Simulations that combine transferable ion-water and ion-ion many-body potentials could directly examine how pairing modifies interfacial ion distributions, surface excesses, and surface-tension increments. This extension would help translate the intrinsic single-ion propensities identified here into predictions for finite-concentration alkali-metal halide solutions. It would also provide access to molecular ensembles under more experimentally relevant conditions and enable direct comparisons with surface-sensitive measurements such as vibrational sum-frequency generation (vSFG) spectroscopy.

More broadly, the same framework can be applied across a larger matrix of cation-anion combinations, concentrations, interfaces, and confined environments. Nuclear quantum effects and enhanced-sampling methods will be important when strong hydrogen bonds, slow exchange, or rare association events control the observable of interest. At the same time, emerging machine-learned interatomic potentials offer opportunities for greater chemical coverage, particularly when local representations are combined with explicit electrostatics and physically meaningful long-range response. Many-body decompositions such as those used here provide a useful diagnostic for evaluating these models, understanding their architectural limitations, and identifying which interactions must be learned explicitly.

The central conclusion of this dissertation is that predictive simulations of aqueous ions require both an accurate potential energy surface and a physically balanced partitioning of the interaction energy. Long-range electrostatics establishes the global organization of an ionic system, but short-range nonadditive interactions and collective solvent response determine how that organization is expressed locally. Treating these contributions consistently provides not only improved numerical accuracy but also a molecular framework for understanding why ions with the same formal charge can behave so differently across bulk solutions, interfaces, and concentrated environments.

Appendix A

Supplementary Figures

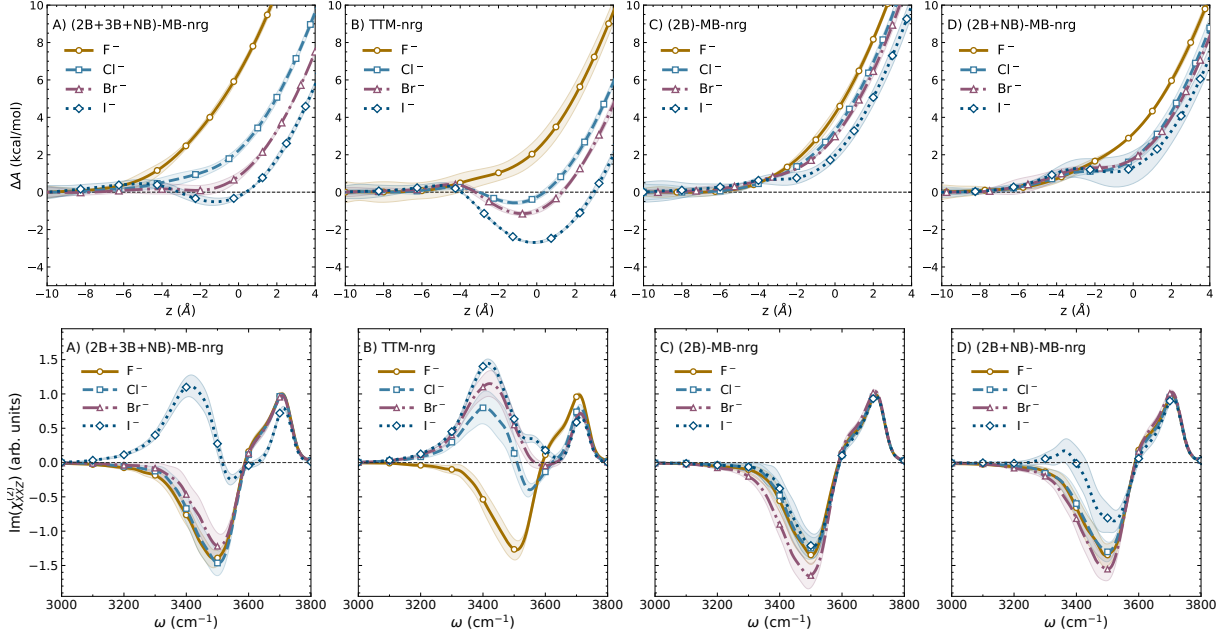


Figure A.1: Helmholtz free-energy profiles (upper panel) and HD-vSFG spectra in the XXZ polarization combination (lower panel) calculated for the single-halide air/water interface using different ion–water PEFs: (A) (2B+3B+NB)-MB-nrg, (B) TTM-nrg, (C) (2B)-MB-nrg, and (D) (2B+NB)-MB-nrg. The many-body dipole moment surface (MB- μ) and polarizability surface (MB- α) were used to compute the dipole moments and polarizability tensors. [107] The second-order susceptibility $\chi_{ijk}^{(2)}(\omega)$ was calculated from the Fourier transform of the dipole moment–polarizability time-autocorrelation function. [114] Nonresonant background contributions and Fresnel factors were not included. The spectra were red-shifted by 175 cm^{-1} to approximately account for nuclear quantum effects. [109] Each spectrum was weighted according to the corresponding PMF, such that configurations in different interfacial regions contribute in proportion to the equilibrium probability of finding the ion at that position. Shaded bands denote the 95% confidence intervals estimated from approximately 100 independent 50-ps trajectories propagated in the NVE ensemble.

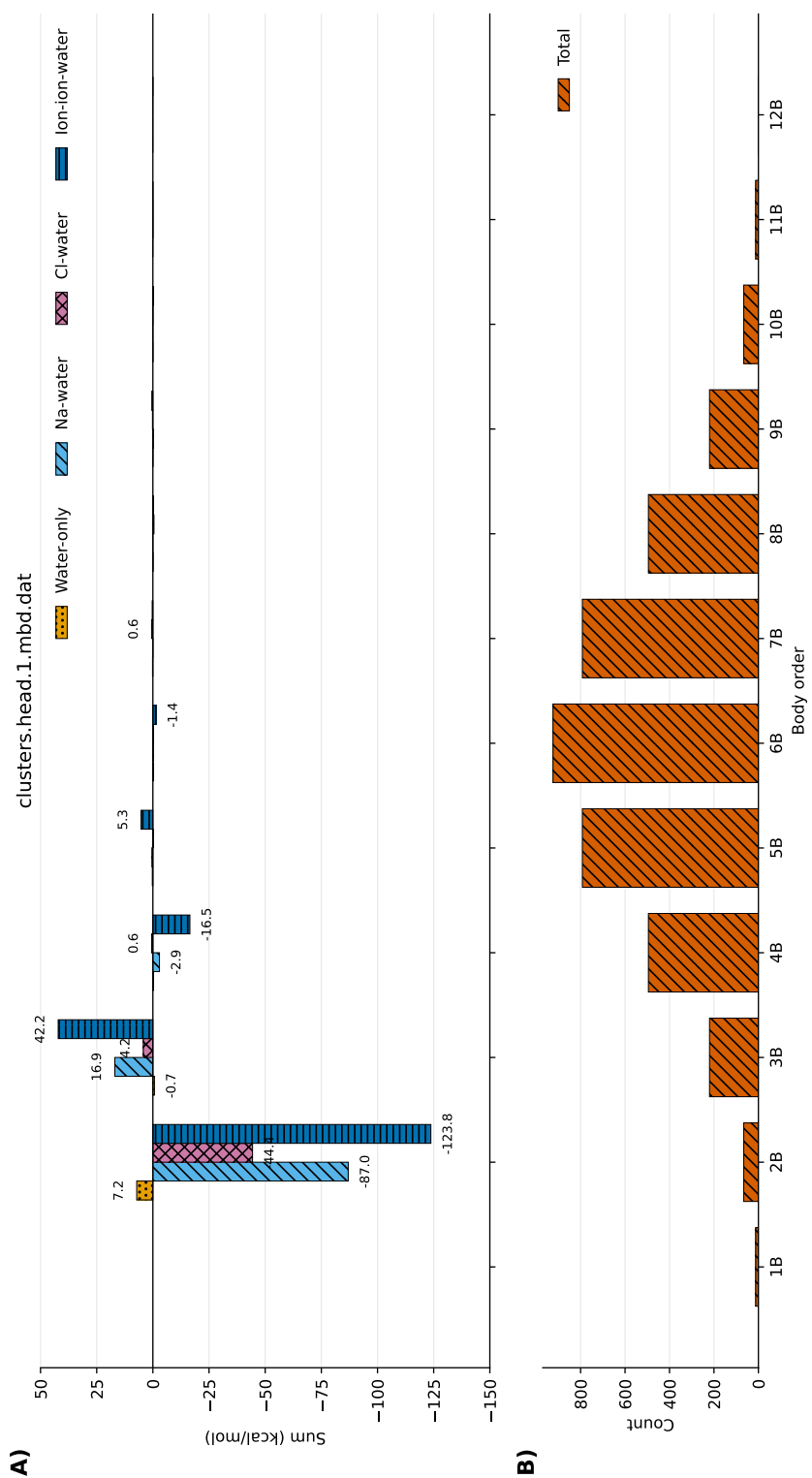


Figure A.2: Full, untruncated many-body decomposition of a Na–Cl–10H₂O cluster using DLPNO-CCSD(T). Mixed-ion contributions persist through 6B and become negligible by 7B.

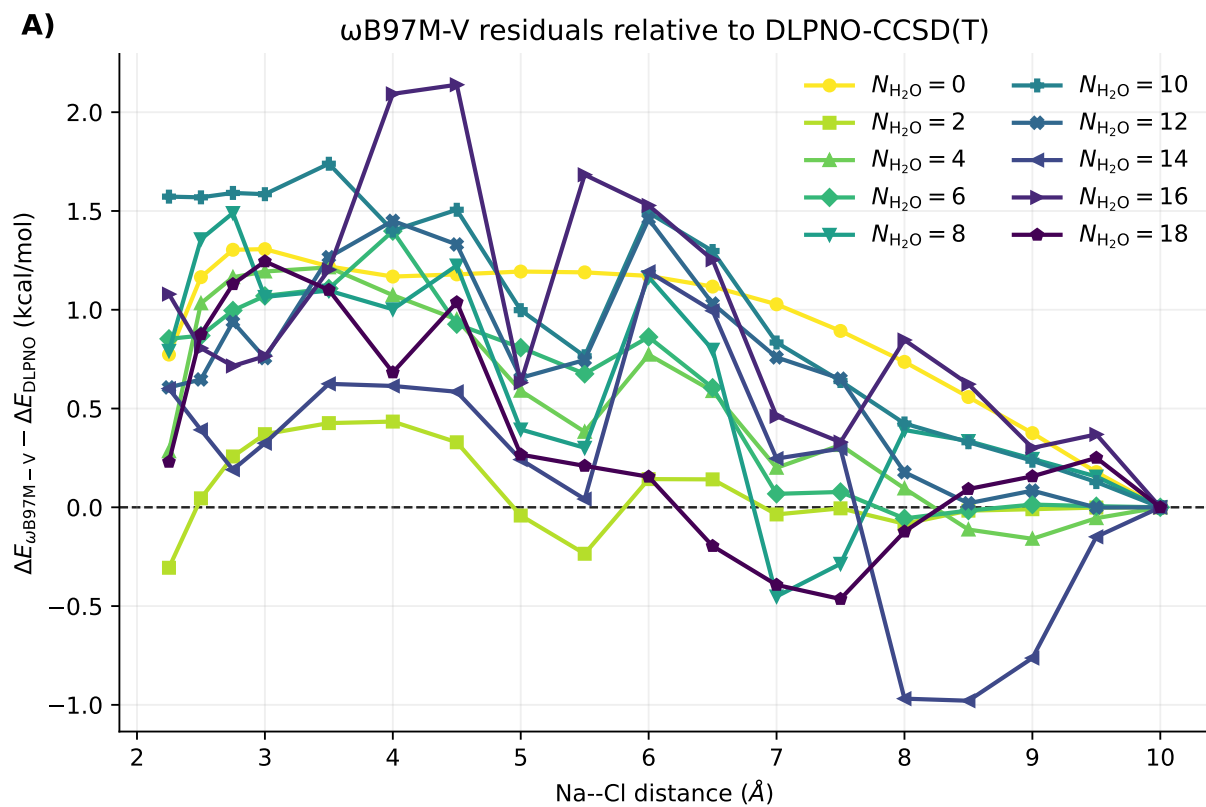


Figure A.3: Comparison of ω B97M-V with DLPNO-CCSD(T) for Na-Cl-H₂O clusters. The ten series represent clusters containing 0, 2, ..., 18 water molecules.

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