i-TTM Model for Ab Initio-Based Ion-Water Interaction Potentials. II. Alkali Metal Ion–Water Potential Energy Functions.

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1 Basis Set Convergence Analysis

Tables 1 and 2 show the basis set convergence analysis for the minimum energy dimers $M^+(H_2O)$ with $M^+ = Na^+$, Rb^+. Tables 3 and 4 show the coordinates of the corresponding dimers. Similar results were obtained for the other ions using the same electronic structure methods.

Table 1 Basis set convergence analysis for $Na^+(H_2O)$ interaction energies without (E_{int}) and with BSSE correction (E_{int}^{BSSE}) and the corresponding BSSE error δE

Method/Basis Set	$Na^+(H_2O)$		
	E_{int}	E_{int}^{BSSE}	δE
CCSD(T)/cc-pCVTZ	-23.502	-23.057	-0.445
CCSD(T)/cc-pCVQZ	-23.863	-23.701	-0.163
CCSD(T)/cc-pCV5Z	-24.010	-23.932	-0.078
CCSD(T)/cc-pCV(TQ)Z	-23.951	-23.857	-0.094
CCSD(T)/cc-pCV(Q5)Z	-24.046	-23.988	-0.058
CCSD(T)-F12b/cc-pCVTZ	-23.954	-23.800	-0.153
CCSD(T)-F12b/cc-pCVQZ	-24.043	-23.997	-0.046
CCSD(T)-F12b/cc-pCV(TQ)Z	-24.070	-24.067	-0.003

Table 2 Basis set convergence analysis for $Rb^+(H_2O)$ interaction energies without (E_{int}) and with BSSE correction (E_{int}^{BSSE}) and the corresponding BSSE error δE

Method/Basis Set	$Rb^+(H_2O)$		
	E_{int}	E_{int}^{BSSE}	δE
CCSD(T)/def2-TZVPP	-16.423	-14.997	-1.426
CCSD(T)/def-2QZVPP	-15.643	-15.216	-0.428
CCSD(T)/def2-(TQ)ZVPP	-15.339	-15.468	0.129

2 Extrapolation to Complete Basis Set Limit

In order to extrapolate the CCSD(T) and CCSD(T)-F12b energies to the complete basis set (CBS) limit, we follow the procedures that have been recommended in references 1, 2 and 3. We here summarize the procedures to facilitate reproduction of our results.

Table 3 Geometry[a] of the $Na^+(H_2O)$ dimer used in the convergence study.

Atom	x / Å	y / Å	z / Å
O	0.000015	1.078408	0.000000
H	0.760368	1.666810	0.000000
H	-0.760650	1.666406	0.000000
Na	0.000015	-1.087316	0.000000

[a] The geometry has been optimized using DFT (ωB97XD) and the aug-cc-pVTZ basis set for all the atoms.

Table 4 Geometry[a] of the $Rb^+(H_2O)$ dimer used in the convergence study.

Atom	x / Å	y / Å	z / Å
O	-0.368124	-1.262052	0.000000
H	0.589706	-1.183277	0.000000
H	-0.671483	-0.350104	0.000000
Rb	-1.904824	-3.601136	0.000000

[a] The geometry has been optimized using DF-MP2 and TZVPP basis set for all atoms.

2.1 Hartree–Fock reference

As recommended in Ref. 1, we employ an exponential ansatz to extrapolate the Hartree–Fock (HF) reference energy,

$$E_{HF}^{(\zeta)} = E_{HF}^{CBS} + Ae^{-\alpha\zeta}, \quad (1)$$

where ζ is the cardinal number of the basis set. For the exponent α, we employ the recommended value of 1.63 for correlation consistent basis sets [1], while the coefficient A is obtained from two calculations with different basis sets,

$$A = \frac{E_{HF}^{(\zeta_1)} - E_{HF}^{(\zeta_2)}}{e^{-\alpha\zeta_1} - e^{-\alpha\zeta_2}}. \quad (2)$$

For the def2-nZVPP basis sets, we employ the exponents that have been optimized for a slightly different extrapolation [3]

according to

$$E_{\rm HF}^{(\zeta)} = E_{\rm HF}^{\rm CBS} + Ae^{-\tilde{\alpha}\sqrt{\zeta}}. \quad (3)$$

2.2 CCSD(T)-F12b correlation energy

For the extrapolation of the CCSD(T)-F12b correlation energies, we follow the recommendations from Ref. 2. A power-law-based extrapolation procedure is employed,

$$E_{\rm corr}^{(\zeta)} = E_{\rm corr}^{\rm CBS} + A\zeta^{-\beta}, \quad (4)$$

which leads to a two-point extrapolation according to

$$E_{\rm corr}^{\rm CBS} = \frac{\zeta_1^{\beta} E_{\rm corr}^{(\zeta_1)} - \zeta_2^{\beta} E_{\rm corr}^{(\zeta_2)}}{\zeta_1^{\beta} - \zeta_2^{\beta}}. \quad (5)$$

Different values are employed for β to extrapolate the CCSD-F12 correlation energy and the triples contribution. Table 5 shows the values of the parameters α, $\beta^{(\rm CCSD-F12)}$ and $\beta^{(\rm T)}$ that were used to extrapolate the CCSD(T)-F12b energies for the $Li^+(H_2O)$ and $Na^+(H_2O)$ dimers.

Table 5 Extrapolation parameters for CCSD(T)-F12b dimer interaction energies (see Refs. 1,2)

M^+	Basis Set	ζ_1	ζ_2	α	$\beta^{(\rm CCSD-F12)}$	$\beta^{(\rm T)}$
Li^+	cc-pCVnZ	3	4	1.63	4.26	3.20
Na^+	cc-pCVnZ	3	4	1.63	4.26	3.20

2.3 CCSD(T) correlation energy

In order to obtain the CBS limit of the CCSD(T) correlation energy, we parameters β that were optimized[3] both for def2-nVZPP basis sets and also correlation consistent basis sets using the power-law-based extrapolation procedure from equation (5). Table 6 shows the values of the parameters $\tilde{\alpha}$ and β that we employed for extrapolation of HF energies and CCSD(T) correlation energies for $K^+(H_2O)$, $Rb^+(H_2O)$, and $Cs^+(H_2O)$ dimers.

Table 6 Extrapolation parameters for CCSD(T) dimer interaction energies (see Ref. 3)

M^+	Basis Set	ζ_1	ζ_2	$\tilde{\alpha}$	β
Na^+	cc-pCVnZ	4	5	9.19	3.00
K^+	cc-pwCVnZ	3	4	5.46	3.05
Rb^+	def2-QZVPP	3	4	7.88	2.98
Cs^+	def2-QZVPP	3	4	7.88	2.98

2.4 Many-Body decompositions

We present in Tables 7 - 10 the many body decomposition corresponding to $M^+(H_2O)_n$, for $M^+ = Li^+$ (Table 7), K^+ (Table 8), Rb^+ (Table 9, and Cs^+ (Table 10).

References

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Table 7 CCSD(T)(-F12b), i-TTM, and AMOEBA 2009 many-body decompositions (in kcal/mol) for $Li^+(H_2O)_n$ clusters. The energies are divided in contributions from water-water interactions, and from ion-water interactions.

n	symmetry	k-body term	CCSD(T)(-F12b)	i-TTM	AMOEBA 2009
1	C_{2v}	$2B_{total}$	-34.81	-35.28	-33.41
2	D_{2d}	$2B_{ion\text{-}wat}$	-69.37	-70.32	-66.54
		$2B_{wat\text{-}wat}$	1.27	1.28	1.40
		$2B_{total}$	-68.10	-69.04	-65.14
		$3B_{total}$	3.36	6.10	3.62
3	D_3	$2B_{ion\text{-}wat}$	-103.44	-104.87	-99.13
		$2B_{wat\text{-}wat}$	4.45	4.38	5.07
		$2B_{total}$	-98.99	-100.49	-94.06
		$3B_{ion\text{-}wat}$	11.34	20.81	12.72
		$3B_{wat\text{-}wat}$	-0.28	-0.32	-0.24
		$3B_{total}$	11.06	20.49	12.48
		$4B_{total}$	-0.58	-1.20	0.56
4	S_4	$2B_{ion\text{-}wat}$	-135.95	-137.81	-130.25
		$2B_{wat\text{-}wat}$	9.69	9.55	10.88
		$2B_{total}$	-126.26	-128.26	-119.37
		$3B_{ion\text{-}wat}$	23.90	40.18	25.30
		$3B_{wat\text{-}wat}$	-1.30	-1.44	-1.11
		$3B_{total}$	22.60	38.74	24.09
		$4B_{ion\text{-}wat}$	-2.58	-4.62	-2.33
		$4B_{wat\text{-}wat}$	0.07	0.08	0.05
		$4B_{total}$	-2.51	-4.54	-2.28
		$5B_{total}$	0.12	0.25	0.10

Table 8 CCSD(T)(-F12b), i-TTM, and AMOEBA 2009 many-body decompositions (in kcal/mol) for $K^+(H_2O)_n$ clusters. The energies are divided in contributions from water-water interactions, and from ion-water interactions.

n	symmetry	k-body term	CCSD(T)(-F12b)	i-TTM	AMOEBA 2009
1	C_{2v}	$2B_{total}$	-17.97	-17.02	-17.63
2	D_{2d}	$2B_{ion\text{-}wat}$	-35.81	-34.07	-35.11
		$2B_{wat\text{-}wat}$	0.55	0.55	0.58
		$2B_{total}$	-35.26	-33.52	-34.53
		$3B_{total}$	1.38	1.47	1.26
3	C_2	$2B_{ion\text{-}wat}$	-42.71	-40.86	-41.60
		$2B_{wat\text{-}wat}$	-6.52	-6.33	-5.96
		$2B_{total}$	-49.23	-47.19	-47.56
		$3B_{ion\text{-}wat}$	-1.35	-1.12	-1.64
		$3B_{wat\text{-}wat}$	0.91	0.91	0.91
		$3B_{total}$	-0.44	-0.21	-0.73
		$4B_{total}$	0.42	0.51	0.54
4	C_2	$2B_{ion\text{-}wat}$	-60.28	-57.75	-58.85
		$2B_{wat\text{-}wat}$	-5.08	-4.89	-4.50
		$2B_{total}$	-65.36	-62.64	-63.35
		$3B_{ion\text{-}wat}$	1.44	2.01	0.94
		$3B_{wat\text{-}wat}$	0.93	0.93	0.93
		$3B_{total}$	2.37	2.94	1.87
		$4B_{ion\text{-}wat}$	0.37	0.41	0.48
		$4B_{wat\text{-}wat}$	-0.01	-0.02	-0.02
		$4B_{total}$	0.36	0.39	0.46
		$5B_{total}$	-0.03	-0.02	-0.02

Table 9 CCSD(T)(-F12b), i-TTM, and AMOEBA 2009 many-body decompositions (in kcal/mol) for $Rb^+(H_2O)_n$ clusters. The energies are divided in contributions from water-water interactions, and from ion-water interactions.

n	symmetry	k-body term	CCSD(T)(-F12b)	i-TTM	AMOEBA 2009
1	C_{2v}	$2B_{total}$	-15.47	-14.82	-14.11
2	D_{2d}	$2B_{ion\text{-}wat}$	-30.84	-29.66	-28.48
		$2B_{wat\text{-}wat}$	0.46	0.46	0.48
		$2B_{total}$	-30.38	-29.20	-28.00
		$3B_{total}$	1.14	1.17	1.12
3	C_2	$2B_{ion\text{-}wat}$	-37.13	-35.83	33.95
		$2B_{wat\text{-}wat}$	-6.59	-6.53	-6.26
		$2B_{total}$	-43.72	-42.36	-40.21
		$3B_{ion\text{-}wat}$	-1.63	-1.44	-1.84
		$3B_{wat\text{-}wat}$	0.90	0.89	0.88
		$3B_{total}$	-0.73	-0.55	-0.96
		$4B_{total}$	0.36	0.44	0.48
4	C_2	$2B_{ion\text{-}wat}$	-52.39	-50.58	-48.39
		$2B_{wat\text{-}wat}$	-5.39	-5.35	-5.04
		$2B_{total}$	-57.78	-55.93	-53.43
		$3B_{ion\text{-}wat}$	0.74	1.07	-0.50
		$3B_{wat\text{-}wat}$	0.91	0.89	-0.90
		$3B_{total}$	1.65	1.96	1.40
		$4B_{ion\text{-}wat}$	0.33	0.38	0.43
		$4B_{wat\text{-}wat}$	-0.01	-0.01	-0.01
		$4B_{total}$	0.32	0.37	0.42
		$5B_{total}$	-0.01	-0.01	-0.02

Table 10 CCSD(T)(-F12b), i-TTM, and AMOEBA 2009 many-body decompositions (in kcal/mol) for $Cs^+(H_2O)_n$ clusters. The energies are divided in contributions from water-water interactions, and from ion-water interactions.

n	symmetry	k-body term	CCSD(T)(-F12b)	i-TTM	AMOEBA 2009
1	C_{2v}	$2B_{total}$	-13.90	-12.54	-12.66
2	C_s	$2B_{ion\text{-}wat}$	-25.14	-22.54	-22.51
		$2B_{wat\text{-}wat}$	-2.28	-2.30	-1.76
		$2B_{total}$	-27.42	-24.84	-24.27
		$3B_{total}$	0.76	0.81	0.73
3	C_2	$2B_{ion\text{-}wat}$	-33.59	-30.76	-30.63
		$2B_{wat\text{-}wat}$	-6.68	-6.61	-6.39
		$2B_{total}$	-40.27	-37.37	-37.02
		$3B_{ion\text{-}wat}$	-1.91	-1.72	-2.07
		$3B_{wat\text{-}wat}$	0.90	0.89	0.88
		$3B_{total}$	-1.01	-0.83	-1.19
		$4B_{total}$	0.38	0.40	0.45
4	C_2	$2B_{ion\text{-}wat}$	-47.26	-43.37	-43.60
		$2B_{wat\text{-}wat}$	-5.70	-5.65	-5.42
		$2B_{total}$	-52.96	-49.02	-49.02
		$3B_{ion\text{-}wat}$	0.56	0.55	0.21
		$3B_{wat\text{-}wat}$	0.90	0.88	0.89
		$3B_{total}$	1.46	1.43	1.10
		$4B_{ion\text{-}wat}$	0.37	0.37	0.42
		$4B_{wat\text{-}wat}$	-0.01	-0.01	-0.01
		$4B_{total}$	0.36	0.36	0.41
		$5B_{total}$	-0.02	-0.01	-0.02