Study of Lithium Cation in Water Clusters: Based on Atom-Bond Electronegativity Equalization Method Fused into Molecular Mechanics

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We present a potential model for Li^+−water clusters based on a combination of the atom-bond electronegativity equalization and molecular mechanics (ABEEM/MM) that is to take ABEEM charges of the cation and all atoms, bonds, and lone pairs of water molecules into the intermolecular electrostatic interaction term in molecular mechanics. The model allows point charges on cationic site and seven sites of an ABEEM-7P water molecule to fluctuate responding to the cluster geometry. The water molecules in the first sphere of Li^+ are strongly structured and there is obvious charge transfer between the cation and the water molecules; therefore, the charge constraint on the ionic cluster includes the charged constraint on the Li^+ and the first-shell water molecules and the charge neutrality constraint on each water molecule in the external hydration shells. The newly constructed potential model based on ABEEM/MM is first applied to ionic clusters and reproduces gas-phase state properties of $Li^+(H_2O)_n$ ($n = 1-6$ and 8) including optimized geometries, ABEEM charges, binding energies, frequencies, and so on, which are in fair agreement with those measured by available experiments and calculated by ab initio methods. Prospects and benefits introduced by this potential model are pointed out.

1. Introduction

Clusters of metal cations with water represent a first approximation to the phenomenon of aqueous solution and play important roles in many chemical and physical processes and in the understanding of intermolecular interactions.[1] The lithium cation, the smallest monopositive cation, playing widespread and diverse roles in biology, medical, and technical applications,[2−4] has been the primary test case for studies on metal cations. An accurate description of interaction potentials and structures for cation−water clusters is very important and necessary. The dissociation energies of losing one H_2O for gas-phase clusters $Li^+(H_2O)_n$ ($n = 1-6$) have been determined by a variety of experimental techniques.[5,6] Dzidic and Kebarle[5] have reported the successive enthalpy changes for $Li^+(H_2O)_n$ ($n = 2-6$) and extrapolated them backward to obtain the enthalpy value for $Li^+(H_2O)$. Rodgers and Armentrout[6] have determined the dissociation energies of $Li^+(H_2O)_n$ ($n = 1-6$) directly by kinetic-energy-dependent collision-induced dissociation experiments in a guided ion mass spectrometer.

The continuous development of computers is making it feasible to study the structures and energies of quite large clusters using ab initio methods. Ab initio studies of Li^+−water clusters, employing various levels of theory and extended basis sets, can predict intermolecular interactions and yield theoretical structures as well as other static nature.[7−20] Feller et al.[10,12,13] performed calculations on $Li^+(H_2O)_n$ ($n = 1-6$) using extended basis sets and various correction methods with up to MP2 for the larger clusters and confirmed that the lowest-energy cluster has four water molecules bound to the cation. Feller[15] also demonstrated that the seventh water prefers the third hydration sphere for $Li^+(H_2O)_7$. Hashimoto and Kamimoto[17] have investigated the structure, stability, and electronic state of $Li^+(H_2O)_n$ ($n = 1-6$ and 8) by an ab initio molecular orbital method and found that the interior structure where the Li^+ is surrounded by four water molecules in the first shell and more in the second shell is the most stable configuration. The geometries and vibrational frequencies of $Li^+(H_2O)_n$, $n = 4$, 5, 6, 8, and 18 have been calculated at various levels up to MP2/6-31+G*.[18] All of these available ab initio calculations on the binding energies and structural properties of Li^+−water clusters may guide us in developing accurate models for Li^+−water interactions which can be applied to studies of larger clusters and bulk solution.

There are a broad variety of cation−water potentials furnished with very different parameters, yielding widely spread results for the calculated properties. A major part of Li^+−water potentials reported in the literature are of a standard Lennard-Jones[21−33] and Coulomb term, whereas the nonelectrostatic short-range part is also represented by including terms with other powers of $1/r^{34-36}$ or more complicated forms with exponential short-range repulsion.[37−45] However, to the best of our knowledge, the electrostatic interactions are modeled by point charges on well-defined sites in the molecular frame and have not been devised explicitly before.

The electronegativity equalization method (EEM) based on the density functional theory (DFT) has recently been parametrized and validated for atomic charge calculations by Langenaeker and co-workers.[46,47] To date, there are several EEM-type formalisms such as a nonempirical electronegativity equalization scheme by Proft et al.,[48] electronegativity equalization in the process of bond formation by Cioslowski et al.,[49] in the form of a charge equilibration method (Qeq) by Rappé and

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Goddard,[50] and the chemical potential equalization method by York and Yang[51] and by Itskowitz and Berkowitz,[52] and so on. Moreover, Patel et al. have built CHARMM fluctuating charge force field,[53] and Rick et al. have developed dynamical fluctuating charge (FQ) force fields,[54,55] etc.

The goal of the present study is to construct a new Li^+−water interaction potential, based on the atom-bond electronegativity method (ABEEM)[56−62] fused into molecular mechanics (MM). Our group has recently developed the ABEEM-7P water potential model[56,57] by use of the combination of ABEEM and MM. In this paper, we further investigate and construct the Li^+−water potential based on ABEEM/MM. The Li^+−water potential has its advantages in the following respects: (1) the combination of ABEEM and MM can perfect the electrostatic interaction in that ABEEM can deal well with the charges of the cation and water molecules and their fluctuating in response to the different local environment; (2) in the molecular mechanics, the van der Waals interaction takes the lithium−oxygen interaction and the lithium−hydrogen interaction into account by 12−6 Lennard-Jones interaction energy. The Li^+−water interaction potential, together with the ABEEM-7P model,[56,57] is applied to describe the properties of a Li^+ cation in water. We first explore and test the newly constructed potential model for ionic clusters $\mathrm{Li}^+(\mathrm{H_2O})_n$ (n = 1−6 and 8).

The rest of this work is organized as follows. In section 2, we describe a combination of the atom-bond electronegativity equalization method and molecular mechanics (ABEEM/MM) to construct the potential model for ionic clusters. In section 3, we present the details of the parametrization. The results and discussion are given in section 4, and conclusions are summarized in section 5.

2. Methodology

2.1. Outline of ABEEM for Describing a Cation in Water. The atom-bond electronegativity equalization method has been applied successfully to calculate the energy, the charge distribution, etc., of a large organic or biological molecule.[58−62] Recently, it has also been applied to the water system[56] and its molecular dynamics simulation.[57] When extending this model to describe a cation in water, the energy expression should be modified to some extent to describe the cation−water interaction energy and rewritten as eq 1

In eq 1. E^*_{ia}, μ^*_{ia}, η^*_{ia}, and q_{ia} are the valence-state energy, the valence-state chemical potential, the valence-state hardness, and the partial charge of atom a in molecule i, respectively; $E^*_{i(a-b)}$, $\mu^*_{i(a-b)}$, $\eta^*_{i(a-b)}$, and $q_{i(a-b)}$ are the valence-state energy, the valence-state chemical potential, the valence-state hardness, and the partial charge of bond $a-b$ in molecule i, respectively; $E^*_{i(lp)}$, $\mu^*_{i(lp)}$, $\eta^*_{i(lp)}$, and $q_{i(lp)}$ are the valence-state energy, the valence-state chemical potential, the valence-state hardness, and the partial charge of lone pair lp in molecule i, respectively; and E^*_I, μ^*_I, η^*_I, q^*_I, and q_I are the valence-state energy, the valence-state chemical potential, the valence-state hardness, the valence-state charge, and the partial charge of cation I, respectively. R is the distance between the charge sites, for example, $R_{ia,ib}$, $R_{i(a-b),i(g-h)}$, and $R_{i(lp),i(lp')}$ are the distances between atoms a and b, the distance between bonds $a-b$ and $g-h$, and the distance between lone pairs lp and lp' in molecule i, respectively, in which the bond charge is located on the point that partitions the bond length according to the ratio of covalent atomic radii of two bonded atoms, and the lone-pair center is placed on the point that is 0.74 Å far from the oxygen nucleus. $k_{ia,i(g-h)}$ and $k_{ia,i(lp)}$ are regarded as adjustable parameters; k is an overall correction coefficient for the intramolecular interaction in the model; $k_{lp,H}(R_{iH,j(lp)})$ is related to the separation between the hydrogen atom belonging to molecule i and the lone-pair belonging to molecule j in the hydrogen bond interaction region (HBIR); $k_{I,i(lp)}$ is an adjustable parameter used to describe the interaction between the cation and the lone-pair in the hydrated ion (HI), a more complex representative supermolecule entity in aqueous solution comes from the old electrochemical concept.[63] In eq 1, the first {} term represents the intramolecular energy for water molecules and the cation, whereas the second {} term represents the water−water intermolecular interaction energy and the cation−water interaction energy.

The effective electronegativity of an atom, a chemical bond, a lone pair, or a cation is identified as the negative of the corresponding chemical potential, i.e., the partial derivative of total energy E with respect to the corresponding electron number or partial charge: $\mu_i = (\partial E/\partial N_i)_{R,N_j} = -(\partial E/\partial q_i)_{R,q_j} = -\chi_i$. Thus, based on eq 1, the effective electronegativities of atom a, bond $a-b$, lone pair lp in water molecule i, and cation I are expressed respectively as

$$
\begin{aligned}
E = \Bigg\{ \sum_{i=1}^{N_{mol}} \Bigg[& \sum_{a}\left(E^*_{ia} - \mu^*_{ia}q_{ia} + \eta^*_{ia}q^2_{ia}\right) + \sum_{lp}\left(E^*_{i(lp)} - \mu^*_{i(lp)}q_{i(lp)} + \eta^*_{i(lp)}q^2_{i(lp)}\right) + \sum_{a-b}\left(E^*_{i(a-b)} - \mu^*_{i(a-b)}q_{i(a-b)} + \eta^*_{i(a-b)}q^2_{i(a-b)}\right) + \\
& \sum_{g-h}\sum_{a(=g,h)} \frac{k_{ia,i(g-h)}q_{ia}q_{i(g-h)}}{R_{ia,i(g-h)}} + \sum_{a}\sum_{lp(\in a)} \frac{k_{ia,i(lp)}q_{ia}q_{i(lp)}}{R_{ia,i(lp)}} + k\Bigg(\frac{1}{2}\sum_{a}\sum_{b(\neq a)}\frac{q_{ia}q_{ib}}{R_{ia,ib}} + \frac{1}{2}\sum_{a-b}\sum_{g-h(\neq a-b)}\frac{q_{i(a-b)}q_{i(g-h)}}{R_{i(a-b),i(g-h)}} + \frac{1}{2}\sum_{lp}\sum_{lp'(\neq lp)}\frac{q_{i(lp)}q_{i(lp')}}{R_{i(lp),i(lp')}} + \\
& \sum_{g-h}\sum_{a(\neq g,h)}\frac{q_{ia}q_{i(g-h)}}{R_{ia,i(g-h)}} + \sum_{a}\sum_{lp(\notin a)}\frac{q_{ia}q_{i(lp)}}{R_{ia,i(lp)}} + \sum_{lp}\sum_{a-b}\frac{q_{i(a-b)}q_{i(lp)}}{R_{i(a-b),i(lp)}}\Bigg)\Bigg] + \left[\mathrm{E}^*_I - \mu^*_I(q_I - q^*_I) + \eta^*_I(q_I - q^*_I)^2\right]\Bigg\} + \\
\sum_{i=1}^{N_{mol}}\Bigg\{\sum_{j=1(\neq i)}^{N_{mol}}\Bigg[& \sum_{\substack{H\in i\\(H,lp\,\mathrm{in\,HBIR})}}\sum_{lp\in j} k_{lp,H}(R_{iH,j(lp)})\frac{q_{iH}q_{j(lp)}}{R_{iH,j(lp)}} + \Bigg(\frac{1}{2}\sum_{a}\sum_{b}\frac{q_{ia}q_{jb}}{R_{ia,jb}} + \frac{1}{2}\sum_{a-b}\sum_{g-h}\frac{q_{i(a-b)}q_{j(g-h)}}{R_{i(a-b),j(g-h)}} + \frac{1}{2}\sum_{lp}\sum_{lp'}\frac{q_{i(lp)}q_{j(lp')}}{R_{i(lp),j(lp')}} + \sum_{g-h}\sum_{a}\frac{q_{ia}q_{j(g-h)}}{R_{ia,j(g-h)}} + \\
& \sum_{\substack{a\\(a\neq H,H\,\mathrm{in\,HBIR}\\ \mathrm{and}\,lp\,\mathrm{not\,in\,HBIR})}}\sum_{lp}\frac{q_{ia}q_{j(lp)}}{R_{ia,j(lp)}} + \sum_{lp}\sum_{a-b}\frac{q_{i(a-b)}q_{j(lp)}}{R_{i(a-b),j(lp)}}\Bigg)\Bigg] + \Bigg[\sum_{lp(inHI)}k_{I,i(lp)}\frac{q_Iq_{i(lp)}}{R_{I,i(lp)}} + \Bigg(\sum_{a}\frac{q_Iq_{ia}}{R_{I,ia}} + \sum_{a-b}\frac{q_Iq_{i(a-b)}}{R_{I,i(a-b)}} + \sum_{lp(notinHI)}\frac{q_Iq_{i(lp)}}{R_{I,i(lp)}}\Bigg)\Bigg]\Bigg\}. \qquad (1)
\end{aligned}
$$

$$\chi_{ia} = \chi_{ia}^{*} + 2\eta_{ia}^{*}q_{ia} + C_{ia}\sum_{a-b} q_{i(a-b)} + D_{ia}\sum_{lp(\in a)} q_{i(lp)} + k\left(\sum_{b(\neq a)}\frac{q_{ib}}{R_{ia,ib}} + \sum_{g-h(\neq a-b)}\frac{q_{i(g-h)}}{R_{ia,i(g-h)}} + \sum_{lp(\notin a)}\frac{q_{i(lp)}}{R_{ia,i(lp)}}\right) + \sum_{j\neq i}\left[\sum_{\substack{lp\\ a=H\\ Hlp \text{ in HBIR}}} k_{lp,H}(R_{ia,j(lp)})\frac{q_{j(lp)}}{R_{ia,j(lp)}} + \left(\sum_{b}\frac{q_{jb}}{R_{ia,jb}} + \sum_{g-h}\frac{q_{j(g-h)}}{R_{ia,j(g-h)}} + \sum_{\substack{lp\\ lp \text{ notin}\\ \text{HBIR}}}\frac{q_{j(lp)}}{R_{ia,j(lp)}}\right)\right] + \frac{q_I}{R_{ia,I}} \tag{2a}$$

$$\chi_{i(a-b)} = \chi_{i(a-b)}^{*} + 2\eta_{i(a-b)}^{*}q_{i(a-b)} + C_{i(a-b),ia}q_{ia} + D_{i(a-b),ib}q_{ib} + k\left(\sum_{g(\neq a,b)}\frac{q_{ig}}{R_{i(a-b),ig}} + \sum_{g-h(\neq a-b)}\frac{q_{i(g-h)}}{R_{i(a-b),i(g-h)}} + \sum_{lp}\frac{q_{i(lp)}}{R_{i(a-b),i(lp)}}\right) + \sum_{j\neq i}\left(\sum_{g}\frac{q_{jg}}{R_{i(a-b),jg}} + \sum_{g-h(\neq a-b)}\frac{q_{j(g-h)}}{R_{i(a-b),j(g-h)}} + \sum_{lp}\frac{q_{j(lp)}}{R_{i(a-b),j(lp)}}\right) + \frac{q_I}{R_{i(a-b),I}} \tag{2b}$$

$$\chi_{i(lp)} = \chi_{i(lp)}^{*} + 2\eta_{i(lp)}^{*}q_{i(lp)} + C_{i(lp)}q_{ia[\in i(lp)]} + k\left(\sum_{g(\notin lp)}\frac{q_{ig}}{R_{i(lp),ig}} + \sum_{g-h}\frac{q_{i(g-h)}}{R_{i(lp),i(g-h)}} + \sum_{lp'(\neq lp)}\frac{q_{i(lp')}}{R_{i(lp),i(lp')}}\right) + \sum_{j\neq i}\left[\sum_{\substack{a\\ a=H\\ H,lp \text{ in HBIR}}} k_{lp,H}(R_{i(lp),ja})\frac{q_{ja}}{R_{i(lp),ja}} + \left(\sum_{\substack{g\\ g\neq H\\ (H \text{ in HBIR})}}\frac{q_{jg}}{R_{i(lp),jg}} + \sum_{g-h}\frac{q_{j(g-h)}}{R_{i(lp),j(g-h)}} + \sum_{lp'}\frac{q_{j(lp')}}{R_{i(lp),j(lp')}}\right)\right] + \left\{\begin{matrix} k_{l,i(lp)}\dfrac{q_I}{R_{i(lp),I}} \text{ (if } lp \text{ is in HI)} \\ \text{or} \\ \dfrac{q_I}{R_{i(lp),I}} \text{ (if } lp \text{ is not in HI)} \end{matrix}\right\} \tag{2c}$$

$$\chi_I = \chi_I^{*} + 2\eta_I^{*}(q_I - q_I^{*}) + \sum_{i}\left[\sum_{lp(inHI)} k_{I,i(lp)}\frac{q_{i(lp)}}{R_{I,i(lp)}} + \left(\sum_{a}\frac{q_{ia}}{R_{I,ia}} + \sum_{a-b}\frac{q_{i(a-b)}}{R_{I,i(a-b)}} + \sum_{lp(notinHI)}\frac{q_{i(lp)}}{R_{I,i(lp)}}\right)\right] \tag{2d}$$

where $\chi_{ia}^{*} = -\mu_{ia}^{*}$, $\chi_{i(a-b)}^{*} = -\mu_{i(a-b)}^{*}$, and $\chi_{i(lp)}^{*} = -\mu_{i(lp)}^{*}$ are the valence-state electronegativities of atom *a*, bond *a*−*b*, and lone pair *lp* in molecule *i*, respectively. $\chi_I^{*} = -\mu_I^{*}$ is the valence-state electronegativity of cation *I*. $C_{i(a-b),ia} = k_{ia,i(a-b)}/R_{ia,i(a-b)}$, $D_{i(a-b),ib} = k_{ib,i(a-b)}/R_{ib,i(a-b)}$, C_{ia}, D_{ia}, $C_{i(lp)}$, and $k_{I,i(lp)}$ are regarded as adjustable parameters.

For heterogeneous system such as ionic clusters, the region charges are also not independent variables since there is a charge conservation constraint. The Li^+ has made some water molecules in the first hydration shell strongly polarized and there is charge transfer between the Li^+ and the near water molecules which can be analyzed and proved by previously reported Mulliken charges of small clusters $Li^+(H_2O)_n$.[64,65] Moreover, Taube experimentally observed more than forty years ago:[66] “The point of view is this: cations, perhaps all the simple ones, exert forces sufficiently strong on water molecules held in the first sphere of hydration, to make these distinguishable from other water molecules, which may also be affected. A general goal is to learn the limits for which such a distinction between ‘first sphere’ and remaining solvent is possible.” This old statement emphasizes the different types of water molecules that are present in aqueous solution, and this viewpoint has guided the work for developing the methodology based on the use of the flexible hydrated ion.[67] In the present work, guided by above viewpoint, the charge constraint on this system includes two parts:

(1) The cation and the water molecules in its first hydration shell, i.e., the hydrated ion (HI), is constrained to be charged, allowing charge transfer within the first-shell water molecules and the cation

$$q_I + \sum_{i=1}^{N_{W1}}\left(\sum_{a}^{N_a} q_{ia} + \sum_{a-b}^{N_{a-b}} q_{i(a-b)} + \sum_{lp}^{N_{lp}} q_{i(lp)}\right) = q_{\text{bare}} \tag{3a}$$

(2) For other water molecules, each water molecule is constrained to be neutral, so there is no intermolecular charge transfer between them

$$\sum_{a}^{N_a} q_{ia} + \sum_{a-b}^{N_{a-b}} q_{i(a-b)} + \sum_{lp}^{N_{lp}} q_{i(lp)} = 0 \ (i = N_{W1} + 1, N_{W1} + 2, ..., N_{\text{mol}}) \tag{3b}$$

For this kind of constraint, the electronegativity equalizations have difference for the two parts:

(1) With the charge transfer within the cation and the water molecules in its first hydration shell, the chemical potentials of the cation and all atoms, bonds, lone pairs of the first-shell water molecules are equal

$$\chi_I = \chi_{i\alpha} = \chi_{j\beta} = \cdots = \chi_{i(\alpha-\beta)} = \chi_{j(\gamma-\delta)} = \cdots = \chi_{i(lp)} = \chi_{j(lp)} = \cdots = \overline{\chi}_{HI} \ (i, j = 1, 2, ..., N_{W1}) \tag{4a}$$

(2) For other water molecules without intermolecular charge transfer, the chemical potentials of an atom, a bond, and a lone

pair are equal within a water molecule

$$\chi_{i\alpha} = \chi_{i(\alpha-\beta)} = \chi_{i(lp)} = \cdots = \bar{\chi}_i$$

$$\chi_{j\alpha} = \chi_{j(\alpha-\beta)} = \chi_{j(lp)} = \cdots = \bar{\chi}_j \; (i, j = N_{W1} + 1, N_{W1} + 2, ..., N_{\text{mol}}) \quad (4b)$$

In eqs 3 and 4, q_{bare} is the total charge of bare cation, and for Li^+, q_{bare} is equal to 1; N_{W1} is the number of water molecules in the first hydration shell; N_{mol} is the total number of water molecules in this system; $\bar{\chi}_{HI}$ denotes the mean electronegativity of the cation and the first-shell water molecules under the influence of the surrounding water molecules. The selection of the size of the charged constraint region for the model is probably the most crucial decision and the region should include the complete first hydration shell around the lithium ion. In the studied ionic clusters, the maximum distance between the Li^+ and the H atom in the first shell is less than 3.0 Å. To include the complete first shell water molecules not only in ionic clusters but also in an aqueous solution of Li^+, the range of 0.3 Å is added. Thus, the radius of the charged constraint region is 3.3 Å and the lithium cation is the center of the region, and this value is similar to the radius of a QM region.[68] The above equations will be solved and discussed respectively in this paper.

2.2. Potential Model Based on ABEEM/MM. In molecular mechanics (MM) calculations, the Li^+-water interaction is written as a Lennard-Jones and Coulomb term, i.e.

$$E_{IW} = \sum (E_{\text{vdw}} + E_{\text{elec}}) \quad (5)$$

For van der Waals interaction, we use standard 12−6 Lennard-Jones potential

$$E_{\text{vdw}} = \sum_a 4\epsilon_{I,a}\left[\left(\frac{\sigma_{I,a}}{r_{I,a}}\right)^{12} - \left(\frac{\sigma_{I,a}}{r_{I,a}}\right)^{6}\right] \quad (6)$$

where $\epsilon_{I,a}$ and $\sigma_{I,a}$ are the Lennard-Jones well depth and diameter parameters for the Li^+ and atom a, respectively, and $r_{I,a}$ is the distance between the Li^+ and atom a. The Lennard-Jones parameters $\epsilon_{I,a}$ and $\sigma_{I,a}$are obtained using the combination rules, $\epsilon_{I,a} = (\epsilon_I \epsilon_a)^{1/2}$, $\sigma_{I,a} = 1/2(\sigma_I + \sigma_a)$, where I means lithium cation and a represents oxygen atom or hydrogen atom. For the Coulomb interaction, the cation−water interaction energy in the last term of eq 1 represents the cation−water electrostatic interaction incorporating the interaction between the charges on atoms, bonds, lone pairs of water molecules, and the charge on the cation; therefore, the implementation of ABEEM in a force field is to take the cation−water interaction part of the last term in eq 1 into eq 5; that is, we calculate the cation−water electrostatic interaction E_{elec} of eq 5 by using ABEEM charges. Then, we can get the concrete form of the cation−water potential based on ABEEM/MM in eq 7

$$E_{Iw} = \sum_i \left\{ \sum_a 4\epsilon_{I,ia}\left[\left(\frac{\sigma_{I,ia}}{r_{I,ia}}\right)^{12} - \left(\frac{\sigma_{I,ia}}{r_{I,ia}}\right)^{6}\right] + \left[\sum_{lp(\text{in HI})} k_{I,i(lp)} \frac{q_I q_{i(lp)}}{R_{I,i(lp)}} + \left(\sum_a \frac{q_I q_{ia}}{R_{I,ia}} + \sum_{a-b} \frac{q_I q_{i(a-b)}}{R_{I,i(a-b)}} + \sum_{lp(\text{not in HI})} \frac{q_I q_{i(lp)}}{R_{I,i(lp)}} \right) \right] \right\} \quad (7)$$

In the present work, we exploit the ABEEM-7P model[56,57] to describe water properties. The ABEEM-7P model assumes that the water molecule is composed of seven charge centers and is allowed the vibration of bond length and bond angle. At the equilibrium geometry of a water molecule, the bond length of O−H and the bond angle of H−O−H are set to their experimental values, 0.9572 Å and 104.52°, respectively, and the lone-pair center is 0.74 Å far from the oxygen nucleus and with an intervening angle of 109.47°. The ABEEM-7P water potential is expressed as

$$E_w = \sum_{\text{bonds}} E_b + \sum_{\text{angles}} E_\theta + \sum_{\text{non-bonded}} (E_{\text{vdw}} + E_{\text{elec}}) \quad (8)$$

where the Morse potential is used to represent the O−H bond stretching, the harmonic potential is employed to represent the H−O−H angle bending, and the Lennard-Jones interaction between water molecules involves oxygen−oxygen interaction, hydrogen−hydrogen interaction, and oxygen−hydrogen interaction, whereas the electrostatic interaction between water molecules is taken from the water−water intermolecular interaction energy in the last term of eq 1. A detailed description of the derivation of water potential can be found in the literature.[56,57] Then, the total potential energy of the cation/water system is expressed as

In eq 9, the O−H bond dissociation energy D is 529.6 kcal/mol and the angle force constant f_θ is 34.05 kcal/mol deg^2, which are available in refs 56 and 57, and q is the charge calculated from the ABEEM method. First, we use eqs 2−4 to compute the charges of the cation and all of the atoms, bonds, and lone pairs of water molecules. Then, we use eq 9 to compute the total potential energy of this system. When there is a change of bond, angle, and relative position of water molecules, or a change of the relative position between the cation and water molecules, we recalculate the charges by eqs 2−4 from time to time, then recalculate the total potential energy by eq 9. Therefore, the combination of ABEEM and MM can not only picture properties with fully fluctuating charges without loss of accuracy in the solvation description of a cation in water but also describe the cation−water interaction explicitly. The CPU time required for the calculation is about two times larger than the usual MM method.

3. Calibration of Parameters

Though only one cation enters water molecules, the hydrogen-bonding network structure of water molecules is interrupted to some extent. Therefore, we should reconsider the intermolecular interaction and recalibrate the nonbonded potential parameters. Especially, more attention is paid to the interaction between the cation and a water lone pair in the hydrated ion. When the cation is closer to the lone-pair such as in $\text{Li}^+(\text{H}_2\text{O})$ which has been indicated as having some covalent bonding,[5] there is charge distribution overlap. Therefore, an adjusted parameter $k_{I,lp}$ is utilized to describe this kind of interaction between the Li^+ and the near lone pairs and the optimized average value of $k_{I,lp}$ is 0.96. By calculating the structural properties and binding energies of Li^+−water clusters and comparing them with the available experimental or ab initio results, we have fitted the parameters. The calibrated ABEEM parameters and van der Waals parameters for water and Li^+ are listed in Table 1. Parameters of water are same as in the ABEEM-7P model.[56,57] This means that the ABEEM-7P model can also quite precisely be used to describe the properties of water molecules in ionic clusters. In addition, the Lennard-Jones parameters of Li^+ are similar to that developed by Dang,[69] which represents that our adjusted parameters can also properly reproduce the experimental enthalpy and geometry of the complex $\text{Li}^+(\text{H}_2\text{O})$ formation.

$$\begin{aligned} E = {} & \sum_{\text{bonds}} D[e^{-2\alpha(r-r_{eq})} - 2e^{-\alpha(r-r_{eq})}] + \sum_{\text{angles}} f_\theta(\theta-\theta_{eq})^2 + \sum_i \sum_{j\neq i} \Bigg\{ \sum_a \sum_b 4\epsilon_{ia,jb}\left[\left(\frac{\sigma_{ia,jb}}{r_{ia,jb}}\right)^{12} - \left(\frac{\sigma_{ia,jb}}{r_{ia,jb}}\right)^{6}\right] + \\ & \sum_{\substack{H\in i\\ (H,lp\text{ in HBIR})}} \sum_{lp\in j} k_{lp,H}(R_{iH,j(lp)}) \frac{q_{iH}q_{j(lp)}}{R_{iH,j(lp)}} + \Bigg[\frac{1}{2}\sum_a\sum_b \frac{q_{ia}q_{jb}}{R_{ia,jb}} + \frac{1}{2}\sum_{a-b}\sum_{g-h}\frac{q_{i(a-b)}q_{j(g-h)}}{R_{i(a-b),j(g-h)}} + \frac{1}{2}\sum_{lp}\sum_{lp'}\frac{q_{i(lp)}q_{j(lp')}}{R_{i(lp),j(lp')}} + \sum_{g-h}\sum_a \frac{q_{ia}q_{j(g-h)}}{R_{ia,j(g-h)}} + \\ & \sum_{\substack{a\\ (a\neq H,H\text{ in HBIR}\\ \text{and } lp\text{ not in HBIR})}} \sum_{lp} \frac{q_{ia}q_{j(lp)}}{R_{ia,j(lp)}} + .\sum_{lp}\sum_{a-b}\frac{q_{i(a-b)}q_{j(lp)}}{R_{i(a-b),j(lp)}}\Bigg]\Bigg\} + \\ & \sum_i \Bigg\{\sum_a 4\epsilon_{I,ia}\left[\left(\frac{\sigma_{I,ia}}{r_{I,ia}}\right)^{12} - \left(\frac{\sigma_{I,ia}}{r_{I,ia}}\right)^{6}\right] + \Bigg[\sum_{lp(\text{in HI})} k_{I,i(lp)}\frac{q_Iq_{i(lp)}}{R_{I,i(lp)}} + \left(\sum_a \frac{q_Iq_{ia}}{R_{I,ia}} + \sum_{a-b}\frac{q_Iq_{i(a-b)}}{R_{I,i(a-b)}} + \sum_{lp(\text{not in HI})}\frac{q_Iq_{i(lp)}}{R_{I,i(lp)}}\right)\Bigg]\Bigg\} \end{aligned} \tag{9}$$

TABLE 1: ABEEM/MM Parameters[a]

	χ^{*b}	$2\eta^*$	C	D	σ(Å)	ϵ (kcal/mol)
H−	2.023	3.774	2.161		3.051	0.044
O−	3.773	26.098	11.493	5.312	2.240	0.012
H−O	5.136	24.767	2.161	11.493		
*lp*O−	3.308	6.692	5.312			
Li$^+$	9.402	45.030			1.506	0.166

[a] χ^*, η^*, *C*, and *D* are the parameters in eqs 2a−d; for the atom H, the parameter *C* stands for $C_{H,H-O}$; for the atom O, the parameter *C* stands for $C_{O,H-O}$ and the parameter *D* stands for $D_{O,lpO}$; for the bond H−O, the parameter *C* stands for $C_{H-O,H}$ and the parameter *D* stands for $D_{H-O,O}$; for the lone-pair of O, the parameter *C* stands for $C_{O,lpO}$. [b] The Pauling electronegativity unit is used.

In the present model, the correction factor *k* takes the same value of 0.57 as in the MEEM and previous ABEEM method,[56−62] but it is only used to describe the intramolecular interaction. Although the ABEEM-7P water model[56,57] has been employed here, the charged system is different from the neutral water system in that the charge density governs the interaction of cation with waters, and the balance of forces determines water structure, electrostatics (water's dipole interacting with cation), and hydrogen bonding (water interacting with neighboring waters).[70] Accordingly, the parameter $k_{lp,H}(R_{lp,H})$ is reparametrized and is different from the pure water system. The Li$^+$ largely perturbs the water's hydrogen bonding network structure and its dynamics and makes water molecules polarized relative to neutral water molecules, which results in increased positive charge of the hydrogen atom in the first shell and strengthens the hydrogen bonding to the water molecule in the second hydration shell. Representative geometries of Li$^+$(H$_2$O)(H$_2$O), Li$^+$(H$_2$O)$_2$(H$_2$O), Li$^+$(H$_2$O)$_3$(H$_2$O), Li$^+$(H$_2$O)$_4$(H$_2$O), and Li$^+$(H$_2$O)$_4$(H$_2$O)$_2$ are chosen, and the corresponding parameter $k_{lp,H}(R_{lp,H})$ is adjusted to make the computed binding energies agree well with the experimental or ab initio results. The refitted expression of $k_{lp,H}(R_{lp,H})$ is as follows:

$$k_{lp,H}(R_{lp,H}) = 0.915 - \frac{0.040}{1 + e^{(R_{lp,H}-1.200)/0.012}} \tag{10}$$

The corresponding graph of $k_{lp,H}(R_{lp,H})$ is depicted in Figure 1.

4. Results and Discussion

In this section, we examine several properties of ionic clusters Li$^+$(H$_2$O)$_n$ (n = 1−6 and 8). In particular, we focus on the results of the most stable clusters since these structures exhibit some interesting characteristics. We present the results from our study on those properties such as optimized geometries, stability, ABEEM charges, total binding energies, successive binding energies, and vibrational frequencies and compare them with the available ab initio and experimental data.

4.1. Geometries of Li$^+$(H$_2$O)$_n$ (n = 1−6 and 8) Clusters. For Li$^+$(H$_2$O)$_n$ (n = 1−6 and 8) clusters, we start with the ab initio geometries and perform a local energy minimization with the BFGS quasi-Newton method[71] in our ABEEM/MM. The optimized geometries of Li$^+$(H$_2$O)$_n$ (n = 1−6 and 8) are shown in Figure 2.

In this paper, the cluster structure of Li$^+$(H$_2$O)$_p$(H$_2$O)$_q$ is denoted by $p + q = n$, where n is the total number of water molecules in the cluster, and p and q are the number of water molecules in the first, external hydration shells, respectively.[17,20] As shown in Figure 2, the most stable structures of Li$^+$(H$_2$O)$_n$ (n = 1−4) are that all water molecules are directly bound to the Li$^+$ without hydrogen bonds, i.e., the isomers IIa through IVa are more stable than the isomers IIb through IVb by 7.5, 4.7, and 1.2 kcal/mol for n = 2, 3, and 4, respectively. For Li$^+$(H$_2$O)$_5$, the 4 + 1 structure with C_2 symmetry, where four water molecules exist in the first hydration shell and one second-shell water molecule is bound to Li$^+$(H$_2$O)$_4$ via two hydrogen bonds forming a cyclic structure, is more stable than the 5 + 0 isomer by 4.4 kcal/mol. In addition, the existence of the local minimum for isomer 5 + 0 is dependent on the calculation levels, and it does not have a stable local minimum at HF/6-31G* and MP2/6-31+G* levels.[18] For Li$^+$(H$_2$O)$_6$, the 4 + 2 structure with D_{2d} symmetry is the most stable isomer, where also four water molecules are in the first shell and two second-shell water molecules form two cyclic structures constructed with hydrogen bonds to the first-shell water molecules. Whereas isomer 6 + 0 is much less stable. The most stable structures of

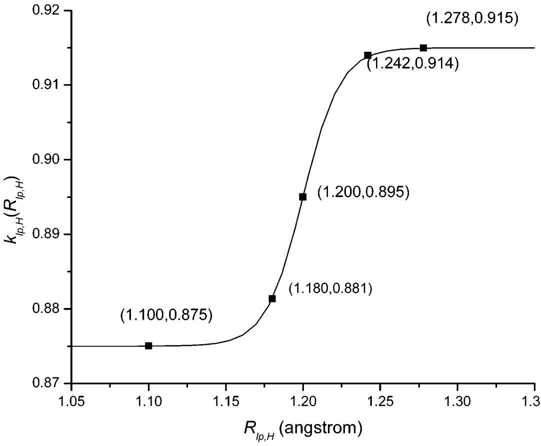

Figure 1. Function $k_{lp,H}(R_{lp,H})$ which corresponds to the distance between the lone-pair and the H atom which will form the hydrogen bond. The fitted data are in parentheses.

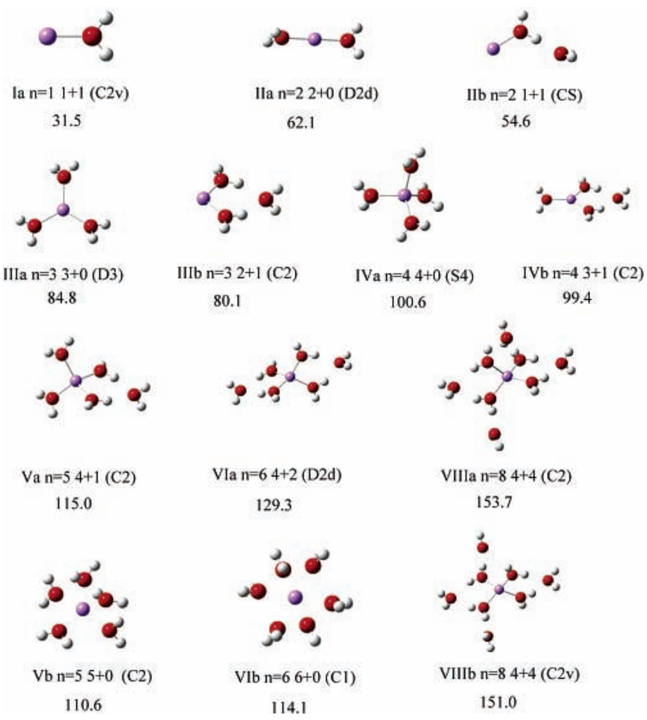

Figure 2. Optimized structures of $Li^+(H_2O)_n$ (n = 1−6 and 8) calculated by our potential model. The total binding energies in kcal/mol are also given.

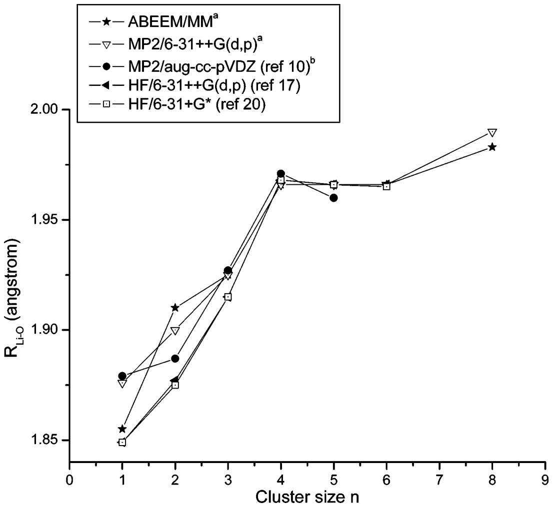

Figure 3. Average distance R_{Li-O} in the first hydration shell with increasing cluster size n, together with the ab initio results. [a]The most stable structures of $Li^+(H_2O)_n$ (n = 1−6 and 8) are used in each size n for the evaluation. [b]With frozen core approximation for n = 1−5.

TABLE 2: Charges for ABEEM-7P Model Water and the Most Stable Structures of $Li^+(H_2O)_n$ (n = 1−4) Calculated by the ABEEM Model

		$Li^+(H_2O)_n$[a]			
	H_2O	$n = 1$	$n = 2$	$n = 3$	$n = 4$
q_{cation}		0.910	0.915	0.921	0.927
q_O	0.112	0.104	0.104	0.101	0.103
q_H	0.290	0.471	0.433	0.405	0.385, 0.381
q_{O-H}	−0.155	−0.142	−0.144	−0.143	−0.146
q_{lp}	−0.191	−0.336	−0.320	−0.299	−0.290, −0.269

[a] The geometries are in Figure 2. q_{cation} is the charge on the site of Li^+, q_O and q_H are the charges on the sites of the atom O and H, q_{O-H} is the charge on the site of the ratio of covalent atomic radii of the atom O and H, q_{lp} is the charge on the site 0.74 Å from the O atom. According to the symmetries of $Li^+(H_2O)_n$, the charge of every site of one water molecule is same as another water molecule in the cluster.

TABLE 3: Charges for the Most Stable Structures of $Li^+(H_2O)_{5,6}$ Calculated by the ABEEM Model[a]

	$Li^+(H_2O)_5$		$Li^+(H_2O)_6$[b]
q_{cation}	0.926	q_{cation}	0.926
$q_{O2,3}$	0.096	$q_{O2,3,11,12}$	0.103
$\mathbf{q_{O4}}$	**0.099**	$\mathbf{q_{O4,17}}$	**0.106**
$q_{O5,6}$	0.099	$q_{H5,7,14,16}$	0.340
$q_{H7,9}$	0.368	$q_{H6,8,13,15}$	0.434
$q_{H8,10}$	0.430	$\mathbf{q_{H9,10,18,19}}$	**0.368**
$\mathbf{q_{H11,12}}$	**0.359**	q_{O2-H5}	−0.148
$q_{H13,15}$	0.359	q_{O2-H6}	−0.142
$q_{H14,16}$	0.371	$\mathbf{q_{O4-H9}}$	**−0.147**
$q_{O2-H7,O3-H9}$	−0.143	q_{lpO2}	−0.284
$q_{O2-H8,O3-H10}$	−0.139	$\mathbf{q_{lpO4}}$	**−0.274**
$\mathbf{q_{O4-H11,12}}$	**−0.144**		
$q_{O5-H13,O6-H15}$	−0.143		
$q_{O5-H14,O6-H16}$	−0.144		
$q_{lpO2,3}$	−0.317		
$q_{lp'O2,3}$	−0.249		
$\mathbf{q_{lpO4}}$	**−0.265**		
$q_{lpO5,6}$	−0.300		
$q_{lp'O5,6}$	−0.260		

[a] The geometries are in Figure 4. q_{cation}, q_O, and q_H are the charges on the sites of cation, O atom, and H atom, q_{O-H} is the charge on the site of the ratio of covalent atomic radii of the O atom and the H atom, q_{lp} is the charges on the site 0.74 Å from the O atom. Charges on the sites of water molecules in the second shell are indicated in boldface. Charge of the bound H atom is indicated in underline. [b] For $Li^+(H_2O)_6$ (D_{2d} symmetry), the value of q_{O2-H5} is same as q_{O3-H7}, $q_{O11-H14}$, $q_{O12-H16}$; the value of q_{O2-H6} is same as q_{O3-H8}, $q_{O11-H13}$, $q_{O12-H15}$; the value of q_{O4-H9} is same as q_{O4-H10}, $q_{O17-H18}$, $q_{O17-H19}$; the value of q_{lpO2} is same as q_{lpO3}, q_{lpO11}, q_{lpO12}; and the value of q_{lpO4} is same as q_{lp17}.

$Li^+(H_2O)_n$ (n = 1−6) optimized by our potential model are similar to recently reported ab initio results.[17,19,20] For $Li^+(H_2O)_8$, as shown in Figure 2, two isomers both have the 4+4 geometry where two water molecules are bound to the isomer VIa and the most stable isomer is the C_2 symmetric configuration. Therefore one conclusion is that the most stable structures of $Li^+(H_2O)_n$ ($n \geqslant 5$) tend to have four first-shell water molecules, which is well consistent with the previous reports.[7−20]

For the most stable isomers, the average distance of Li^+-O with increasing size n is given for the first hydration shell, compared with the ab initio results including our theoretical calculation at the MP2/6-31++G(d,p) level, shown in Figure 3. It was previously noted by ab initio calculations[10,17,20] that the average distance R_{Li-O} is increasing with cluster size n (for $n \leqslant 4$) due to the repulsion of the water ligands and changes slightly for $Li^+(H_2O)_n$ ($n \geqslant 4$) in that the added water molecules are bound to $Li^+(H_2O)_4$ via hydrogen bonds. A similar trend has been established by ABEEM/MM-based potential model. Moreover, the differences between ab initio values and ours are at most ∼0.035 Å for all n. The good accordance with ab initio results in all cases reflects that our potential model can correctly predict the structural properties of clusters $Li^+(H_2O)_n$ (n = 1−6 and 8).

4.2. ABEEM Charges of $Li^+(H_2O)_n$ (n = 1−6) Clusters. We list the ABEEM charges for ABEEM-7P model water and the most stable structures of $Li^+(H_2O)_n$ (n = 1−6) in Tables 2 and 3. For the model water, the negative charges locate on the O−H bond (−0.155) and the lone-pair (−0.191) and the positive charges locate on the O atom (0.112) and the H atom (0.290). In cationic clusters, every water molecule has a different charge distribution because an enhancement of effective dipole moment happens in the cation−water case.

For $Li^+(H_2O)$, the Li^+ makes the water molecule obviously polarized, and less positive charge locates on the O atom, more

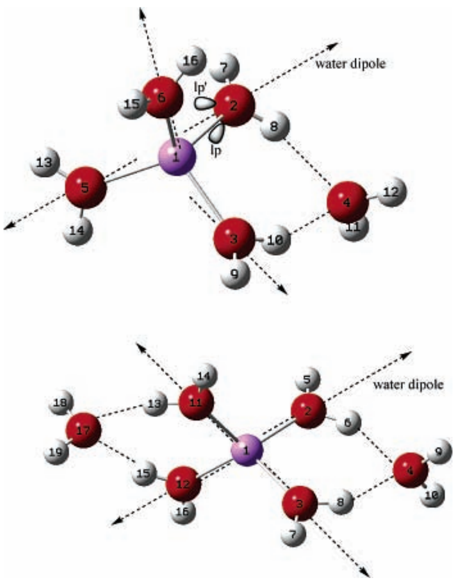

Figure 4. Most stable structures of $Li^+(H_2O)_5$ and $Li^+(H_2O)_6$, together with the water dipole directions of four first-shell water molecules.

positive charge on the H atom, less negative charge on the O−H bond, as well as more negative charge on the lone-pair. It looks that the electron located on OH groups flows up to the lone-pair orbital region and the cation. The obvious charge transfer is 0.090 between the Li^+ and the water molecule in $Li^+(H_2O)$. From $Li^+(H_2O)$ to $Li^+(H_2O)_4$, the charge transfer and absolute values of charges located on the H atom and the lone-pair of a water molecule reduce with the increasing number of water molecules. For clusters $Li^+(H_2O)_5$ and $Li^+(H_2O)_6$ (see Figure 4 and Table 3), the second-shell water molecules are still polarized compared with an isolated water molecule. Furthermore, the charges of bound H atoms are 0.430 and 0.434, much larger than the charges of free H atoms (0.368 and 0.340). On the other hand, the arrangement of the water molecules in the second hydration shell directly influences the structure and charge distribution of the first-shell water molecules. For example, in the $Li^+(H_2O)_6$ cluster, because the alignment of the second-shell water molecules has good symmetry, the ABEEM charges of the first shell water molecules are in good order and every water molecule orients its dipole to the cation (see Figure 4). However, in the $Li^+(H_2O)_5$ cluster, the two lone pairs on the oxygen atom have different charges [such as −0.317 (*lp*) and −0.249 (*lp*′)], which manifests that the lone-pair with more negative charge orients to the Li^+, i.e., the orientation of the first-shell water molecule deviates from the water dipole due to the unsymmetrical arrangement of the second-shell water molecule. From the geometries and charges of cationic clusters, we can predict the orientation of the water molecules in the first hydration shell of Li^+ in aqueous ionic solution: it may be a water lone pair toward the Li^+ because of the disorder of the external water molecules.

From ABEEM charges of $Li^+(H_2O)_n$, we can see the necessity of the division of charged/neutral regions. In cluster $Li^+(H_2O)$, the Li^+−water pair and the water molecule both affect their electron clouds. For clusters $Li^+(H_2O)_n$ ($n = 2-4$), there is not only the cation−water interaction but also the water−water interaction which all affect the electron clouds of the Li^+ cation and the water molecules; therefore, the total positive charge (+1) is distributed in the whole cluster though mainly on the Li^+. For larger clusters $Li^+(H_2O)_5$ and $Li^+(H_2O)_6$, due to the saturation of the first hydration shell, the added water molecules (more than four) lie in the second hydration shell via hydrogen bonds. The charges of the water molecules in the second hydration shell are different from that in the first hydration shell and the partial charge of Li^+ changes slightly for $Li^+(H_2O)_n$ ($n \geqslant 5$), which reflects that the Li^+ and the first-shell water molecules have strong interaction and affect the electron clouds for each other with a corresponding large amount of charge transfer between them. For the external water molecules, this kind of effect is very small and there is almost no intermolecular charge transfer. Therefore, it is reasonable to partition the whole system into two kinds of constraint regions: the charged constraint region for the cation and the first-shell water molecules, and charge neutral constraint regions for other water molecules. All of the regions have a complementary and cooperative effect.

To summarize, the charges of the cation and the water molecules depend on the geometries of the clusters. In classical molecular mechanics, the electrostatic interactions are modeled by fixed partial charges, which are inappropriate because fixed partial charges cannot reflect the redistribution with the changed ambient environment. Whereas fluctuating charges are very effective and important in the calculation of the interaction energy. The ABEEM model can deal well with the inhomogeneous system and give reasonable fluctuating charges; furthermore, we can obtain the cation−water interaction energy quite precisely.

4.3. Binding Energies. From our optimized geometries, we calculate the total binding energies (ΔE_n) of all isomers and the successive binding energies ($\Delta E_{n,n-1}$) of the most stable structures of $Li^+(H_2O)_n$ by the newly constructed potential model, in terms of the following formulas:

$$-\Delta E_n = E[\mathrm{Li}^+(\mathrm{H_2O})_n] - E[\mathrm{Li}^+] - nE[\mathrm{H_2O}] \quad (11)$$

$$-\Delta E_{n,n-1} = E[\mathrm{Li}^+(\mathrm{H_2O})_n] - E[\mathrm{Li}^+(\mathrm{H_2O})_{n-1}] - E[\mathrm{H_2O}] \quad (12)$$

As shown in Table 4, the calculated total binding energies of all isomers by the ABEEM/MM-based potential agree well with the ab initio results at the MP2/6-311++G(2d,2p)//MP2/6-31++G(d,p) level with counterpoise-correction (CPC). For the most stable structures of $Li^+(H_2O)_n$ ($n = 1-6$) and isomer 4 + 4 with C_{2v} symmetry, our results are also consistent with previously reported results at the MP2/6-31++G(d,p)//HF/6-31++G(d,p) level obtained by Hashimoto et al.[17] From the total binding energies of all isomers, we can conclude that the most stable structures of $Li^+(H_2O)_n$ ($n = 1-4$) are the direct addition of water molecules binding to the Li^+ and hydrogen bond between water molecules is weaker than Li^+−water bonding. However, for $Li^+(H_2O)_n$ ($n \geqslant 5$), the most stable isomer has four inner water molecules. As shown in Table 5, the reducing trend of the successive binding energies with cluster size reflects the progressive saturation in bonding properties of the Li^+ as well as the formation of the first shell at $n = 4$. The successive binding energies of $Li^+(H_2O)_5$ (14.4 kcal/mol) and $Li^+(H_2O)_6$ (14.3 kcal/mol) are higher than the double typical hydrogen bond energies, which is due to not only the formation of two hydrogen bonds via two lone pairs of a water molecule in the second hydration shell with two hydrogen atoms of the first-shell water molecules but also the higher partial charge of the hydrogen atom in a polarized water molecule directly bound to the Li^+ strengthening the hydrogen bond energies. The size dependence of the total binding energies and successive binding energies of the most stable structures of $Li^+(H_2O)_n$ are depicted in Figure 5. The total binding energies of the most stable isomers become

TABLE 4: Total Binding Energies (kcal/mol) of $Li^+(H_2O)_n$ (n = 1−6 and 8), Compared with the ab Initio Results

n	symbol[a]	P+q	Symm.	ABEEM/MM	MP2/6-311++G(2d,2p)//MP2/6-31+G(d,p)[b]	MP2/6-31+G(d,p)//HF/6-31+G(d,p)[c]
1	Ia	1+0	C_{2v}	31.5	32.7	33.8
2	IIa	2+0	D_{2d}	62.1	60.8	63.5
	IIb	1+1	Cs	54.6	50.0	
3	IIIa	3+0	D_3	84.8	83.4	86.5
	IIIb	2+1	C_{2v}	80.1	77.6	
4	IVa	4+0	S_4	100.6	99.9	103.2
	IVb	3+1	C_2	99.4	99.4	
5	Va	4+1	C_2	115.0	115.0	117.1
	Vb	5+0	C_2	110.6	109.3	
6	VIa	4+2	D_{2d}	129.3	129.1	130.3
	VIb	6+0	C_1	114.1	114.3	
8	VIIIa	4+4	C_2	153.7	148.4	
	VIIIb	4+4	C_{2v}	151.0	148.3	148.7

[a] Indicates structures in Figure 2. [b] Counterpoise corrected. [c] Reference 17, with counterpoise corrected.

TABLE 5: Successive Binding Energies (kcal/mol) of the Most Stable Structures of $Li^+(H_2O)_n$ (n = 1−6), Compared with the ab Initio and Experimental Results

		ABEEM/MM	ab initio			expt.[f]	
n	symbol[a]	this work	this work[b]	ref 10[c]	ref 17[e]	ref 5	ref 6
1	Ia	31.5	32.7	33.2	33.8	33.4[g]	32.1
2	IIa	30.6	28.1	29.3	29.7	25.2	26.6
3	IIIa	22.7	22.6	22.8	23.1	20.1	21.7
4	IVa	15.8	16.5	17.5	16.7	15.8	16.4
5	Va	14.4	15.1	15.0	13.9	13.3	13.7
6	VIa	14.3	14.1	12.1[d]	13.1	11.5	14.5

[a] Indicates structures in Figure 2. [b] At the MP2/6-311++G(2d,2p)//MP2/6-31++G(d,p) level, with counterpoise corrected. The most stable isomers are used for each n. [c] At the MP2/aug-cc-pVDZ//MP2/aug-cc-pVDZ level, with frozen core approximation. [d] C_2 symmetry, at the MP2/aug-cc-pVDZ//HF/cc-pVDZ level. [e] At the MP2/6-31++G(d,p)//HF/6-31++G(d,p) level, with counterpoise corrected. [f] We have converted the experimental dissociation enthalpies to the dissociation energies. [g] Extrapolated value.

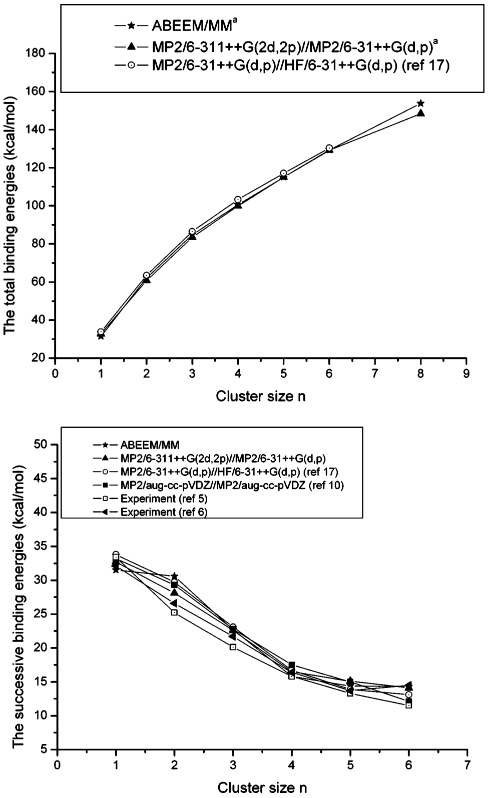

Figure 5. Size dependence of the total binding energies and the successive binding energies. Comparisons with the ab initio and experimental results are also listed. [a]The most stable structures of $Li^+(H_2O)_n$ (n = 1−6 and 8) are used in each size n for the evaluation.

progressively larger and are in good accordance with the ab initio results, whereas the successive binding energies become progressively smaller. Compared with the experimental dissociation energies of $Li^+(H_2O)_n$ (n = 1−6) converted from the experimental dissociation enthalpies,[5,6] as well as the quantum chemistry calculation and the reported ab initio values,[10,17] the successive binding energies calculated by our potential model have good agreement (see Table 5 and Figure 5). These comparisons with higher level calculations and with experimentally measured dissociation energies suggest that ABEEM/MM method provides a reasonable description of the Li^+−water interaction in ionic clusters $Li^+(H_2O)_n$. Thus, the model can correctly predict the successive water binding energies for the cation−water complexes with more water molecules, even for aqueous ionic solution.

4.4. Vibrational Frequencies. Starting from the optimized geometries, we have calculated vibrational frequencies of the water molecules in the most stable structures of $Li^+(H_2O)_n$ (n = 1−4) by the ABEEM/MM-based potential model, compared with vibrational frequencies measured by experiments.[72,73] The results are presented in Table 6. Special attention is given to the large ion-induced frequency shift of the O−H stretching bands, which is also well reproduced by our potential model. As can be seen from Table 6, the lithium cation causes a very strong shift of the O−H stretching modes toward lower wavenumber, whereas the H−O−H bending mode is little influenced. Experimentally, the substantial decrease of vibrational frequencies of the water molecules coordinating to the Li^+ is reported (see Table 6). Particularly, the symmetric stretching frequency of O−H decreases from 3652 [72] to 3440 ± 5 cm^{-1}.[73] Our results agree with this frequency shift. This

TABLE 6: Vibrational Frequencies (cm^{-1}) of ABEEM-7P Model Water and the Water Molecules in the Most Stable Structures, $Li^+(H_2O)$, $Li^+(H_2O)_2$, $Li^+(H_2O)_3$, and $Li^+(H_2O)_4$, Compared with the Experimental Values

normal modes	H_2O	$Li^+(H_2O)$	$Li^+(H_2O)_2$	$Li^+(H_2O)_3$	$Li^+(H_2O)_4$	expt.[a]	$H_2O_{expt.}$[b]
H_2O bend	1367	1401	1396, 1400	1391, 1399	1388−1399	1654 ± 3	1595
O−H sym. str.	3523	3415	3423, 3426	3432, 3438	3437−3446	3440 ± 5	3652
O−H asym. str.	3574	3467	3477	3487, 3487	3493−3494		3756

[a] Reference 73, Raman spectra of aqueous solution of LiCl, 3440 ± 5 cm^{-1} is the O−H stretching mode. [b] Reference 72.

corresponds to the fact that the electron flows from the O−H region to the coordinated lone-pair orbital region as analyzed previously at the part of ABEEM charges. Though vibrational frequencies of the water molecules in ionic clusters are a bit smaller than the recent ab initio[19] and experimental values,[73] the calculated frequency shifts are remarkable enough to reflect how the Li^+ influences the structure of the water molecule bound to it. The shift in the O−H stretching vibration is the largest for $Li^+(H_2O)$, and from $Li^+(H_2O)$ to $Li^+(H_2O)_4$, the shift is diminishing with cluster size *n*, i.e., the interaction between the Li^+ and every water molecule is decreasing with the increasing number of water molecules and the O−H bond length approaches the normal value step by step. In addition, the calculated frequencies for the symmetric stretching of the Li−O mode are 246 cm^{-1} in $Li^+(H_2O)_4$ cluster (S_4 symmetry) and 250 cm^{-1} in $Li^+(H_2O)_4(H_2O)_4$ cluster (C_2 symmetry). Experimentally, the polarized band is at 255 cm^{-1},[74] and the ab initio data[14,18] have provided support for the assignment for the band. Our value is in good agreement with the experimental and ab initio results.

5. Conclusions

For the lithium cation in water clusters, we have constructed an effective Li^+-water interaction potential based on the atom-bond electronegativity equalization method (ABEEM) fused into molecular mechanics (MM), and then applied the Li^+-water potential and the ABEEM-7P model to study cationic clusters $Li^+(H_2O)_n$ ($n = 1-6$ and 8). The model has some improvements compared with others: (1) we exploit the ABEEM-7P water model, a seven-site flexible model with fluctuating charges; (2) we improve the cation−water interaction by taking account of the electrostatic interaction of the cation with seven sites of a water molecule and their changes with the different local environment, moreover, all Lennard-Jones interactions between the Li^+ and the atoms of water molecules have been taken into consideration; (3) based on the old electrochemical concept of the hydrated ion (HI) and the point of view from the experiment, the charge constraint on the whole system can be reasonably partitioned into two interactive cases: the charged constraint on the cation and its adjacent water molecules and the charge neutrality constraint on each water molecule in the external hydration shells. It is done in such a way that the many-body interactions in the hydrated ion are implicitly taken into account and the description of the first-shell water molecules includes polarization and charge-transfer effects, derived from the combination of ABEEM and MM.

Based on the potential model, we have computed several gas-phase properties of clusters $Li^+(H_2O)_n$ ($n = 1-6$ and 8) including the optimal structure, stability, ABEEM charges, total and successive binding energies, harmonic vibrational frequency, and so on, and the results are in fair and reasonable agreement with those measured by the available experiments and ab initio calculations. From the optimal structures and total binding energies, we can obtain the most stable isomers and predict the hydration number of Li^+ to be 4. The ABEEM model can deal well with an inhomogeneous system and give reasonable partial charges depending on the geometry of each cluster, and the charge transfer between the cation and the first-shell water molecules is very explicit. The successive binding energies decrease greatly from $Li^+(H_2O)$ to $Li^+(H_2O)_4$, which can be explained by the progressive saturation in the bonding process of Li^+ and the formation of the first hydration shell at $n = 4$. From the harmonic vibrational frequency analysis, we can know how the cation influences the structure of the first-shell water molecules and makes the stretching mode of O−H bond shift toward lower wavenumber; moreover, the agreement between the calculated Li−O symmetric stretching frequency and the experimental and ab initio results is good.

Overall, the key feature of our potential model is a well geometry-adopted and charge-distributed description for the cation and its close environment. The cation−water interaction potential, together with the ABEEM-7P water model, provides a basis for a detailed study of the mechanism of metallic cation transport, the influence of water molecular structure, and the dynamics on the mobility of cation in aqueous solution, which are in progress.

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