

## *Original Investigations*

### **Non-Additivity in Water-Ion-Water Interactions**

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The three-body system  $\text{Li}^+(\text{H}_2\text{O})_2$  was analyzed to study that non-additive part of the interaction potential which can be obtained by the Hartree–Fock approximation.

For long and intermediate distances the three-body correction was found to be well represented by the induction energy, where bond dipoles are induced on each water molecule by point charges located on the (unpolarizable) lithium ion and on the other molecule respectively; for shorter distances this approximation was corrected by means of an exponential repulsive term. Such a potential model for non-additive interactions was extended to the more general situation  $\text{Li}^+(\text{H}_2\text{O})_n$ , and Monte-Carlo calculations were carried out on clusters containing up to six water molecules; comparison with other simulation results and with available data showed a significantly improved agreement with experiment. Tentative values for  $\Delta H$  are presented for  $n = 7, 8, \dots, 20$ , where experimental data are not available.

**Key words:** Water-ion-water interactions, non-additivity in  $\sim$  – Interaction potential, non-additive part of the  $\sim$  – Clusters,  $\text{Li}^+(\text{H}_2\text{O})_n \sim$

## 1. Introduction

In the study of liquid water [1] and ionic solutions [2, 3] the Monte Carlo, MC, technique has proven most useful to provide reliable structural data. In the above studies the total intermolecular interaction is approximated by pairwise additive potentials,  $V(i, j)$ . It is known, however, that the exact intermolecular interaction for  $n$ -body systems must be expanded in a series of two, three, . . . ,  $n$ -body terms

$$V = \sum V(i, j) + \sum V(i, j, k) + \cdots + \sum V(i, j, \dots, n). \quad (1)$$

From preliminary quantum mechanical studies on small ion-water clusters [4] it appears that the above series converges rather slowly and the terms have alternate signs. The three-body correction has been analyzed elsewhere in detail for the systems lithium ion-water-fluoride ion [5] and water-water-water [6]. In this work we shall limit the analysis of the  $V(i, j, k)$  term, to the contribution present in the Hartree-Fock model, when applied to the whole system water-ion-water; that means in this work we do not include those corrections that are related to electron correlation and can, in principle, be obtained by a full CI on the whole system. For reasons of economy we have examined the  $\text{Li}^+(\text{H}_2\text{O})_2$  system. Preliminary results on the potential energy surface have been reported previously [7].

## 2. Computation of the Three-Body Correction in the Hartree-Fock Approximation

For simplicity in notation, in referring to the  $\text{Li}^+(\text{H}_2\text{O})_2$  system, we shall designate the two water molecules as  $W_1$  and  $W_2$ , the corresponding oxygen atoms as  $O_1$  and  $O_2$  and we shall refer to the plane defined by  $O_1, O_2$  and  $\text{Li}^+$  as *reference plane*. We have considered over two hundred different configurations for the  $\text{Li}W_1W_2$  system. In all configurations we have kept a constant value of 3.55 a.u. for the intermolecular separation ( $O_1-\text{Li}$ ); this value corresponds to the minimum in the  $\text{Li}^+-\text{H}_2\text{O}$  system [8]. As geometrical variables we select  $R(O_2-\text{Li})$  and the angle  $\phi$  defined as  $O_1-\text{Li}-O_2$ .

The configurations analyzed can be grouped into four types. In type 1 the molecular planes of  $W_1$  and  $W_2$  coincide with the reference plane; in type 2 only the plane of  $W_1$  coincides with the reference plane, whereas for  $W_2$  the molecular plane is perpendicular to the reference plane; in type 3 the role of  $W_1$  and  $W_2$  is inverted and in type 4 both molecular planes are perpendicular to the reference plane. The basis sets used in the computations are extended Gaussian basis sets with polarization functions, previously used [8], that yield a total energy for water of  $-76.05538$  a.u. and for  $\text{Li}^+$  an energy of  $-7.2305$  a.u. These values are not far from the Hartree-Fock limit of  $\sim -76.066$  a.u. for water [8] and  $-7.2364$  a.u. for  $\text{Li}^+$  [9]. For each configuration we have computed the Hartree-Fock energy of the pairs  $W_1-W_2$ ,  $\text{Li}-W_1$  and  $\text{Li}-W_2$  (note that the interaction energy for  $\text{Li}-W_1$  needs to be computed only once, since only one geometry is used; it corresponds to a binding interaction of  $-0.05473$  a.u.). The total interaction energy  $I$  for the

Li—W<sub>1</sub>—W<sub>2</sub> system is defined as

$$I = E(\text{Li—W}_1\text{—W}_2) - 2E(\text{W}) - E(\text{Li}^+) \quad (2)$$

with  $E(\text{W}) = E(\text{W}_1) = E(\text{W}_2)$ ; this interaction energy has not been corrected for the basis set superposition error [10], since with the basis set adopted, the error is probably small relative to the quantities in discussion, i.e. the three-body correction. From a previous analysis [6] of the superposition correction in the system (H<sub>2</sub>O)<sub>3</sub>, the superposition error for the geometrical configurations considered here, should go from negligibly small values (at large separation of W<sub>1</sub> and W<sub>2</sub>) to about one tenth of a kilocalory. The non-additive correction to the two-body potentials is given by  $\Delta E$  defined as

$$\Delta E = I - E(\text{Li—W}_1) - E(\text{Li—W}_2) - E(\text{W}_1\text{—W}_2). \quad (3)$$

For each configuration we computed the values of  $R(\text{O}_2\text{—Li})$ , the value of the angle  $\varphi$ ,  $E(\text{Li—W}_2)$ ,  $E(\text{W}_1\text{—W}_2)$ ,  $I$  and  $\Delta E$ . Comparison between the value of  $I$  and the corresponding values of  $\Delta E$  shows that non-additivity correction is definitely not negligible and can be as large as 10 to 15% of the total interaction. For the energy surface of type-1 complexes, see Fig. 1.

### 3. Analysis of the Non-Additivity Correction Term

Non-additivity of intermolecular interactions can be conveniently discussed using the language of perturbation theory. Thus the exchange-type contributions to the interaction energy are non-additive in all orders of the perturbation theory. The first order polarization energy, i.e. the electrostatic energy, is additive. In the second order the polarization energy is composed of two parts: the induction energy which is non-additive, and the dispersion energy which is additive.

As for third-order contributions we shall mention only the Axilrod–Teller term [11], related to the dispersion interaction and not included in the SCF interaction energies. However, in the case of polar systems the Axilrod–Teller term is small and can be neglected. Thus, except for the second order exchange dispersion energy which is believed to be small, the non-additive energy, as calculated in the SCF approach contains all nonadditive contributions to the interaction energy up to second order.

In a recent study of water trimers [6] it has been shown that for this system the non-additive interaction energy can be reasonably well approximated by the non-additivity of the induction energy due to the interaction of atomic point charges and induced bond dipoles. If for this system the non-additive exchange effects are small, they are likely to be relatively still smaller for Li<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> where the induction energy is larger than in (H<sub>2</sub>O)<sub>3</sub>. Hence one may expect that the non-additive contributions to the SCF interaction energy of Li<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> can be approximated by the non-additivity of the induction energy which can be easily evaluated.

Let us treat each water molecule in Li<sup>+</sup>(H<sub>2</sub>O)<sub>2</sub> as a system of two bonds polarized by the atomic charges of another H<sub>2</sub>O molecule and of the Li<sup>+</sup> ion. The Li<sup>+</sup> ion will

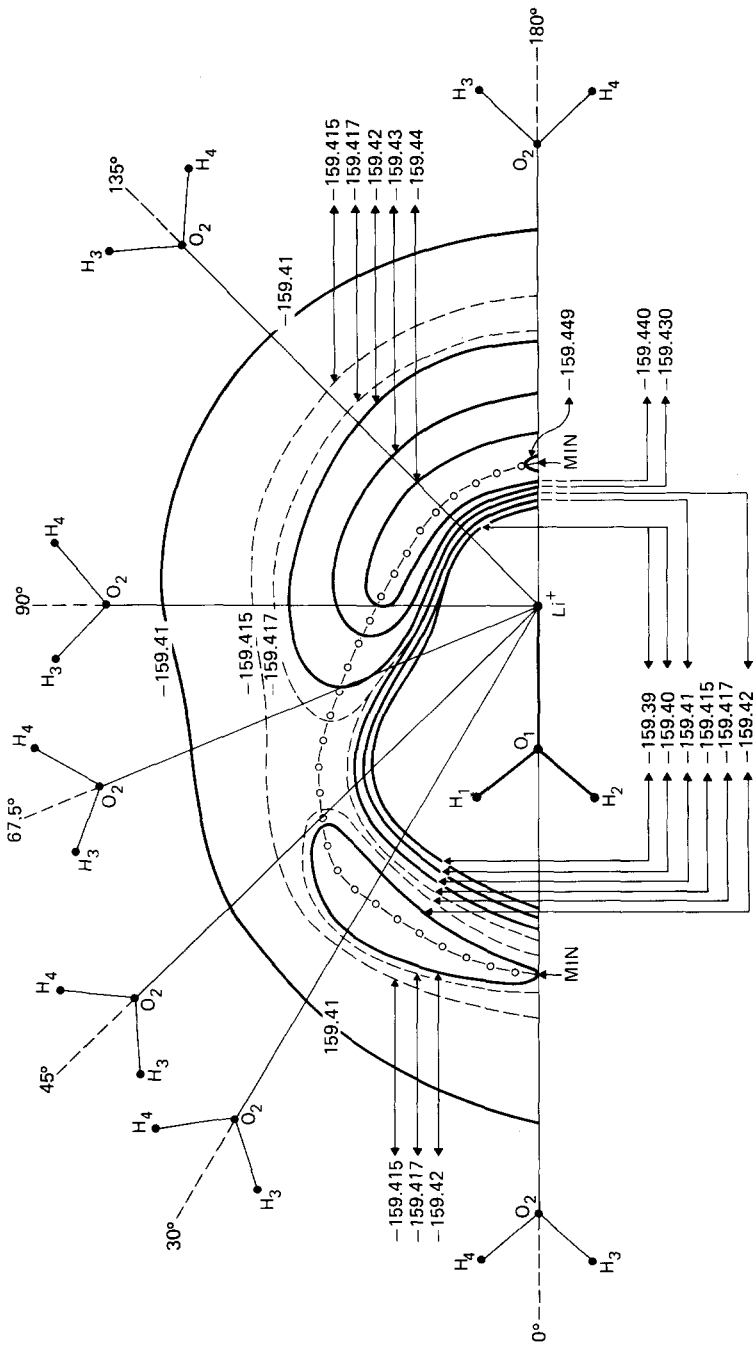


Fig. 1. Hartree-Fock energy surface of the planar  $\text{Li}^+(\text{H}_2\text{O})_2$ , type-1 complexes. Total energies in a.u. (Ref. [7])

be assumed to be unpolarizable. Thus the total induction energy can be expressed as

$$E_{\text{ind}}^{(2)} = E_{\text{ind},A}^{(2)} + E_{\text{ind},B}^{(2)} \quad (4)$$

where  $A$  and  $B$  denote the two  $\text{H}_2\text{O}$  molecules, respectively, and

$$E_{\text{ind},K}^{(2)} = -\frac{1}{2} \sum_{\lambda \in K} [\alpha_{\lambda}^{\text{T}} (\xi_{\lambda} \cdot \xi_{\lambda}) + \delta_{\lambda} (\xi_{\lambda} \cdot \mathbf{e}_{\lambda})^2] \quad (5)$$

where  $\alpha_{\lambda}^{\text{T}}$  and  $\delta_{\lambda}$  denote the transverse polarizability and its anisotropy, respectively, of bond  $\lambda$  in the molecule  $K$ ,  $\xi_{\lambda}$  is the electric field vector at the midpoint of bond  $\lambda$

$$\xi_{\lambda} = \sum_{\mu} \frac{q_{\mu}}{R_{\lambda\mu}^3} \mathbf{R}_{\lambda\mu} \quad (6)$$

where the summation extends over the  $\text{Li}^+$  ion and over atoms of the water molecule different from  $K$ ,  $q_{\mu}$  is the point charge of atom  $\mu$ ;  $\mathbf{R}_{\lambda\mu}$  denotes the radius vector from atom  $\mu$  to the midpoint of the bond  $\lambda$ , and  $\mathbf{e}_{\lambda}$  is the unit vector in the direction of bond  $\lambda$ . From Eqs. (4) to (6) the non-additive component of  $E_{\text{ind}}^{(2)}$  can easily be obtained. It is given by that part of  $E_{\text{ind}}^{(2)}$  which depends on the product  $q_{\mu} \cdot q_{\nu}$  with  $\mu$  and  $\nu$  denoting atoms one of which is  $\text{Li}^+$  and another belongs to the water molecule different from  $K$ . Hence the non-additive interaction energy in the system  $X \cdot A \cdot B$ , with an unpolarizable ion  $X$ , is proportional to the charge  $q_x$  of the ion  $X$ .

In numerical calculations standard values of the bond polarizabilities have been used:  $\alpha_{\text{OH}}^{\text{T}} = 3.91$  and  $\delta_{\text{OH}} = 1.42$  a.u. [12]. For the point charges in  $\text{H}_2\text{O}$  we have used the values  $q_{\text{O}} = -0.682$  and  $q_{\text{H}} = 0.341$ , obtained using an extended basis set [6], and successfully employed in a previous study of the non-additivity of interactions in  $(\text{H}_2\text{O})_3$ .

The results for the four types of configurations of  $\text{Li}^+(\text{H}_2\text{O})_2$  are shown in Figs. 2–5, where the solid lines denote the results of the SCF calculations, and the broken ones have been obtained from Eqs. (4)–(6).

The agreement is seen to be very satisfactory. Appreciable differences between the two sets of results appear only for short distances where the non-additivity of the first order exchange energy, related to the overlap effects, becomes important. Note, however, that the equilibrium  $\text{Li} \cdots \text{O}$  distance in  $\text{Li}^+\text{H}_2\text{O}$  is 3.55 a.u. Hence, the overlap effects not included in the second-order induction energy, become important only for repulsive configurations of  $\text{Li}^+(\text{H}_2\text{O})_2$ .

#### 4. The Short Range Correction

The induction correction as defined by Eq. (4) describes the long- and the intermediate-range behaviour but breaks down at shorter distances. In this distance range the differences between the  $\Delta E$  values calculated by the aid of Eq.

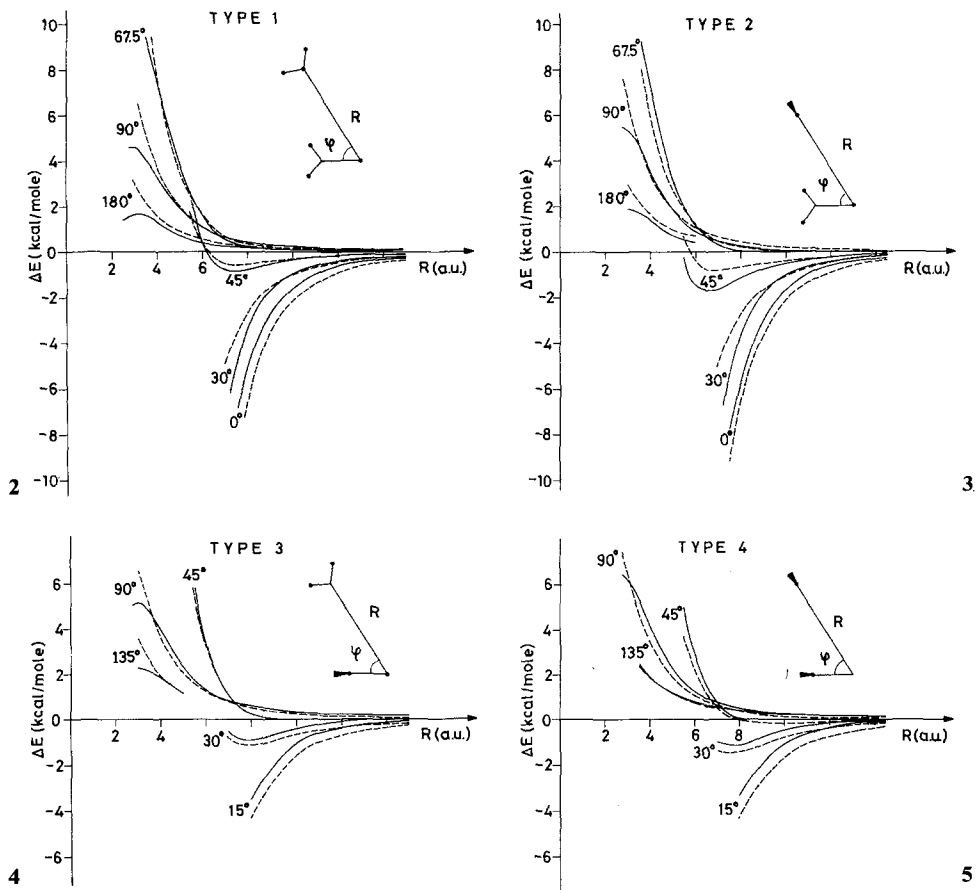


Fig. 2. SCF and induction non-additivity for  $\text{Li}^+(\text{H}_2\text{O})_2$  in type-1 configurations  
 Fig. 3. SCF and induction non-additivity for  $\text{Li}^+(\text{H}_2\text{O})_2$  in type-2 configurations  
 Fig. 4. SCF and induction non-additivity for  $\text{Li}^+(\text{H}_2\text{O})_2$  in type-3 configurations  
 Fig. 5. SCF and induction non-additivity for  $\text{Li}^+(\text{H}_2\text{O})_2$  in type-4 configurations

(3) and those obtained from Eq. (4) can be fitted by a correction term of the form

$$E_{sr} = A \exp \{-C_1 \cdot R(O_1 - O_2) - C_2 \cdot [R(\text{Li}^+ - O_1) + R(\text{Li}^+ - O_2)]\} \quad (7)$$

where the coefficient's values for  $A$ ,  $C_1$  and  $C_2$  are  $1.52 \cdot 10^5$  a.u., 0.19 and 2.24 respectively and the distances  $R$  are expressed in a.u.

## 5. Extension of the Potential Model to a More General Situation and Computer Simulation

Let us rewrite Eq. (6) in the form

$$\xi_{\Lambda} \equiv \xi_{\lambda, K} = \sum_{J \neq K} \mathbf{A} \mathbf{A}_{\Lambda J} \quad (8)$$

where

$$\mathbf{A}_{\Lambda J} = \sum_{\mu \in J} \frac{q_{\mu}}{R_{\Lambda\mu}^3} \mathbf{R}_{\Lambda\mu}.$$

Here the subscript  $\lambda$  refers to a bond in the  $K$ th water molecule, the subscript  $J$  refers to another water molecule and/or to the  $\text{Li}^+$  ion, and the subscript  $\mu$  refers to the point-charge distribution therein; we shall write  $\sum_{\Lambda}$  as a short-hand notation for  $\sum_K \sum_{\lambda \in K}$ .

$$\sum_{\Lambda} (\boldsymbol{\xi}_{\Lambda} \cdot \boldsymbol{\xi}_{\Lambda}) = \sum_{\Lambda} \left( \sum_{J \neq K} \mathbf{A}_{\Lambda J} \right)^2 = \sum_{\Lambda} \sum_{J \neq K} (\mathbf{A}_{\Lambda J} \cdot \mathbf{A}_{\Lambda J}) + \sum_{\Lambda} \sum_J \sum'_L (\mathbf{A}_{\Lambda J} \cdot \mathbf{A}_{\Lambda L}) \quad (10a)$$

and

$$\begin{aligned} \sum_{\Lambda} (\boldsymbol{\xi}_{\Lambda} \cdot \mathbf{e}_{\Lambda})^2 &= \sum_{\Lambda} \left[ \left( \mathbf{e}_{\Lambda} \cdot \sum_{J \neq K} \mathbf{A}_{\Lambda J} \right) \right]^2 = \sum_{\Lambda} \left[ \sum_{J \neq K} (\mathbf{A}_{\Lambda J} \cdot \mathbf{e}_{\Lambda}) \right]^2 \\ &= \sum_{\Lambda} \sum_{J \neq K} (\mathbf{A}_{\Lambda J} \cdot \mathbf{e}_{\Lambda})^2 + \sum_{\Lambda} \sum_J \sum'_L (\mathbf{e}_{\Lambda} \cdot \mathbf{A}_{\Lambda J})(\mathbf{e}_{\Lambda} \cdot \mathbf{A}_{\Lambda L}), \end{aligned} \quad (10b)$$

where the primes in the summation signs mean  $L \neq K$ ,  $L \neq J$ ,  $J \neq K$ ;  $\mathbf{e}_{\Lambda} = \mathbf{e}_{\lambda, K}$  refers to the  $\lambda$ th bond in the  $K$ th water molecule.

We define the non-additive induction energy for our many-body system by

$$\begin{aligned} E_{\text{ind}} = -\frac{1}{2} \left\{ \alpha^{\text{T}} \left[ \sum_{\Lambda} (\boldsymbol{\xi}_{\Lambda} \cdot \boldsymbol{\xi}_{\Lambda}) - \sum_{\Lambda} \sum_{J \neq K} (\mathbf{A}_{\Lambda J} \cdot \mathbf{A}_{\Lambda J}) \right] \right. \\ \left. + \delta \left[ \sum_{\Lambda} (\boldsymbol{\xi}_{\Lambda} \cdot \mathbf{e}_{\Lambda})^2 - \sum_{\Lambda} \sum_{J \neq K} (\mathbf{A}_{\Lambda J} \cdot \mathbf{e}_{\Lambda})^2 \right] \right\} \quad (11) \end{aligned}$$

as for the short-range correction term, we sum Eq. (7) over all pairs of oxygen atoms.

We carried out Monte-Carlo calculations on clusters  $\text{Li}^+(\text{H}_2\text{O})_n$ , with  $n$  ranging from 1 to 6 (which appears to be the largest value for which experimental data are available) and using the following potential models

a) pure two-body potentials:

Hartree–Fock ion–water potential as in Ref. [13] and CI water–water potential from Ref. [14].

b) Same two-body potentials as under a), and many-body terms from Eqs. (7) and (11).

Monte-Carlo calculations were carried out at  $T = 300$  K; the results are reported in Table 1 and Fig. 6, together with experimental data [15, 16] and Monte-Carlo results from Ref. [4], obtained with the same Hartree–Fock ion–water potential as our (Refs. [13]) and a different (Hartree–Fock) water–water potential [17].

The small difference between the two columns of two-body results in Table 1 is due to inclusion of the electron correlation correction in the water–water potential used in our calculations; this term is neglected in Ref. [4].

**Table 1.**  $\text{Li}^+(\text{H}_2\text{O})_n$  clusters; Monte-Carlo results at 300 K; all energies in  $\text{kJ} \cdot \text{mol}^{-1}$ 

| $n$                  | $-U_1/n^a$ | $-U_2/n^b$    | $-U_3/n^c$    | $-1/n \Delta H_{\text{exp}}^d$ |
|----------------------|------------|---------------|---------------|--------------------------------|
| 1                    | 140.2      | 140.1         | —             | 142.3                          |
| 2                    | 134.4      | 134.9         | 125.9         | 125.2                          |
| 3                    | 125.3      | 126.9         | 104.7         | 112.3                          |
| 4                    | 115.1      | 118.0         | 97.2          | 101.4                          |
| 5                    | —          | 104.7         | 88.1          | 92.8                           |
| 6                    | —          | 94.9          | 80.5          | 85.7                           |
| (statistical errors) |            | ( $\pm 0.2$ ) | ( $\pm 0.4$ ) |                                |

<sup>a</sup>  $U_1$ : Results from Ref. [4], two-body potentials.

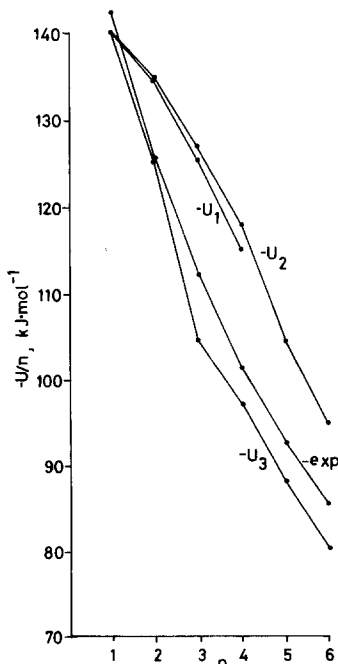
<sup>b</sup>  $U_2$ : Our results, different two-body potentials.

<sup>c</sup>  $U_3$ : Our results, two- and many-body potentials.

<sup>d</sup>  $\Delta H_{\text{exp}}$ : Ref. [15, 16].

Comparison shows that the non-additive interaction brings about a significantly improved agreement with experiment. On the whole, the many-body potential we proposed here, appears to be both physically well-founded and computationally tractable.

In Table 2 we present Monte-Carlo results for  $n = 7, 8, \dots, 19, 20$ , and tentative values for  $\Delta H$ . As apparent in Table 1, for  $2 \leq n \leq 6$ , the experimental  $\Delta H$  is

**Fig. 6.** Comparison between different Monte-Carlo simulation results and with experiment



**Table 2.**  $\text{Li}^+(\text{H}_2\text{O})_n$  clusters; Monte-Carlo results and tentative  $\Delta H$  values at 300°K; all energies in  $\text{kJ} \cdot \text{mol}^{-1}$ 

| $n$                  | $-U_2/n$    | $-U_3/n$    | $-\Delta H/n$ |
|----------------------|-------------|-------------|---------------|
| 7                    | 88.6        | 75.9        | 80.5          |
| 8                    | 81.5        | 70.8        | 74.7          |
| 9                    | 76.2        | 66.8        | 70.2          |
| 10                   | 71.1        | 64.7        | 67.0          |
| 11                   | 68.4        | 61.1        | 63.8          |
| 12                   | 65.2        | 58.5        | 60.9          |
| 13                   | 62.8        | 55.7        | 58.3          |
| 14                   | 61.5        | 53.6        | 56.5          |
| 15                   | 59.5        | 52.7        | 55.2          |
| 16                   | 59.1        | 51.9        | 54.5          |
| 17                   | 55.2        | 51.4        | 52.8          |
| 18                   | 53.3        | 50.4        | 51.4          |
| 19                   | 51.8        | 49.2        | 50.1          |
| 20                   | 50.5        | 47.2        | 48.4          |
| (statistical errors) | ( $\pm 2$ ) | ( $\pm 3$ ) | ( $\pm 5$ )   |

systematically bracketted between the two corresponding values of  $U_2$  and  $U_3$ . For  $n \geq 7$  we obtained estimates of  $\Delta H$  on the basis of  $U_2$  and  $U_3$  results, by calculating the ratio

$$\rho = \frac{\Delta H_{\text{exp}} - U_2}{\Delta H_{\text{exp}} - U_3}, \quad n = 6 \quad (12)$$

and assuming it to maintain the same value up to  $n = 20$ . The statistical error on the estimated  $\Delta H$  is just the sum of the corresponding quantities for  $U_2$  and  $U_3$ , and is likely to be only a lower limit for a realistic estimate of the deviation.

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