

Calculations on the Hydration of Ions

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Several calculations, by both *ab initio* and semiempirical methods, on hydration of ions have been reported.¹⁻⁹

We have performed calculations on $\text{Li}^+\text{H}_2\text{O}$ and $\text{Li}^+(\text{H}_2\text{O})_2$ both by *ab initio* and semiempirical methods using an IBMOL-program^{10,11} and a CNDO/2 program.¹² The purpose has been to calculate the hydration energies and by comparison, investigate the possible utility of the CNDO/2 program for larger hydration aggregates.

In addition to these calculations we have also carried out CNDO/2 calculations

on Li^+ with 4 and 6 water molecules, and on F^- , Cl^- , and Na^+ with 1, 2, 4, and 6 water molecules attached to the ions.

The hydration energy was calculated from:

$$\Delta E = E_{A^\pm(\text{H}_2\text{O})_n} - (E_{A^\pm} + nE_{\text{H}_2\text{O}})$$

where $E_{A^\pm(\text{H}_2\text{O})_n}$ is the calculated energy value for the hydrated ion, E_{A^\pm} is that of the isolated ion, $E_{\text{H}_2\text{O}}$ that of the water molecule, and n is the hydration number.

The geometry of the water molecule was kept constant with the H-O distance 1.0 Å and the H-O-H angle 104.5°. The ion-oxygen distance was varied so that minimum energy was detected. In the cases of more than one oxygen the ion-oxygen distances were varied in a symmetrical fashion so that for 2, 4, and 6 water molecules we had linear, tetrahedral, and octahedral symmetries.

The orbital exponents and expansion coefficients were taken in part from

Table 1. Orbital exponents (α) and expansion coefficients (c).

Type	H		O		Li	
	α	c	α	c	α	c
s	4.50038	0.07048	2714.89	0.004324	284.399	0.005889
	0.681277	0.40789	415.725	0.032265	42.3482	0.044471
	0.151374	1.0	91.9805	0.156410	9.37924	0.194745
			24.4515	1.447813	2.50578	0.474138
			7.22296	1.0	0.733345	1.0
			1.06314	1.0	0.073733	1.0
			0.322679	1.0	0.029787	1.0
p	0.33	1.0	7.75579	0.129373	0.154	1.0
			1.62336	0.481296	0.057	1.0
			0.36503	1.0		
d			0.72	1.0		
			0.1	1.0		

Table 2. Equilibrium values of *ab initio* calculation.

	H_2O - E a.u.	Li^+ - E a.u.	$\text{Li}^+(\text{H}_2\text{O})_n$ - E a.u.	$-\Delta E$ kcal/mol	$d(\text{Li}^+ - \text{O})$ Å
$\text{Li}^+\text{H}_2\text{O}$					
Basis set I	75.885733	7.233138	83.192775	45.5	1.78
Basis set II	75.885733	7.238503	83.197751	32.7	1.81
Basis set III	75.910831	7.238503	83.211633	38.9	1.84
$\text{Li}^+(\text{H}_2\text{O})_2$	75.878167	7.233138	159.12827	88.5	1.79

Veillard¹¹ and from Siegbahn and Roos¹² and are given in Table 1.

In the case of $\text{Li}^+\text{H}_2\text{O}$ three kinds of basis sets were used:

- I (H|3)(O|7,3)(Li+|7)
 II (H|3)(O|7,3)(Li+|7,2)
 III (H|3,1)(O|7,3,2)(Li+|7,2) contracted
 to (H|2,1)(O|4,2)(Li+|4,2)

For the $\text{Li}^+(\text{H}_2\text{O})_2$ case only one basis set was used:

(H|3)(O|7,3)(Li+|7) contracted to
 (H|2)(O|4,2)(Li+|4)

In actual cases d_{Z_2} orbital was added to the oxygen atom. Also in all cases calculations were performed on the Li^+ ion and on the H_2O molecule with the above mentioned geometry.

The results of the *ab initio* calculations are presented in Fig. 1 and Table 2 and of CNDO/2 in Fig. 2, and Table 3. The figures give the total energies as function of ion-oxygen distances. Only the case of Li^+ is presented for CNDO/2 but similar curves were obtained for the other calculations. In the figures the energy is given per water molecule according to:

$$E_{\text{norm}} = \frac{E_{A^\pm(\text{H}_2\text{O})_n} - E_{A^\pm}}{n} + E_{A^\pm}$$

Table 3. Equilibrium values of CNDO/2 calculations.

	$-E_{\text{tot}}$ a.u.	$-AE$ kcal/mol	$d(A^\pm - O)$ Å
$\text{Li}^+\text{H}_2\text{O}$	19.959	45.0	2.38
$\text{Li}^+(\text{H}_2\text{O})_2$	39.914	86.9	2.59
$\text{Li}^+(\text{H}_2\text{O})_4$	78.810	162.8	2.43
$\text{Li}^+(\text{H}_2\text{O})_6$	119.667	216.6	2.49
$\text{Na}^+\text{H}_2\text{O}$	19.939	32.4	2.94
$\text{Na}^+(\text{H}_2\text{O})_2$	39.877	63.8	2.95
$\text{Na}^+(\text{H}_2\text{O})_4$	79.748	124.1	2.95
$\text{Na}^+(\text{H}_2\text{O})_6$	119.611	178.9	2.98
$\text{F}^-(\text{H}_2\text{O})$	47.40590	21.4	2.14
$\text{F}^-(\text{H}_2\text{O})_2$	67.32238	39.4	2.16
$\text{F}^-(\text{H}_2\text{O})_4$	107.14553	69.5	2.24
$\text{F}^-(\text{H}_2\text{O})_6$	146.96814	99.1	2.28
$\text{Cl}^-(\text{H}_2\text{O})$	36.02058	18.8	2.38
$\text{Cl}^-(\text{H}_2\text{O})_2$	55.93481	34.6	2.41
$\text{Cl}^-(\text{H}_2\text{O})_4$	95.76685	70.2	2.37
$\text{Cl}^-(\text{H}_2\text{O})_6$	135.58944	99.8	2.42

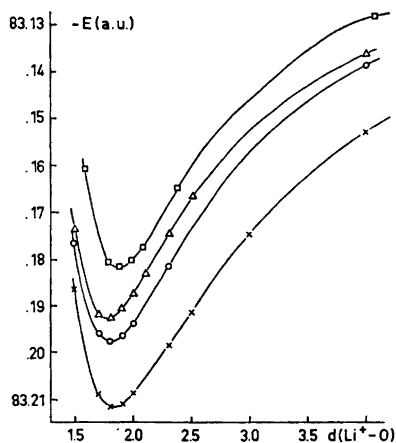


Fig. 1. Energy curves for the $d(\text{Li}^+-\text{O})$ variation of $\text{Li}^+(\text{H}_2\text{O})$ and $\text{Li}^+(\text{H}_2\text{O})_2$. \times : $\text{Li}^+(\text{H}_2\text{O})$ basis set I, \circ : $\text{Li}^+(\text{H}_2\text{O})$ basis set II, Δ : $\text{Li}^+(\text{H}_2\text{O})$ basis set III, \square : $\text{Li}^+(\text{H}_2\text{O})_2$.

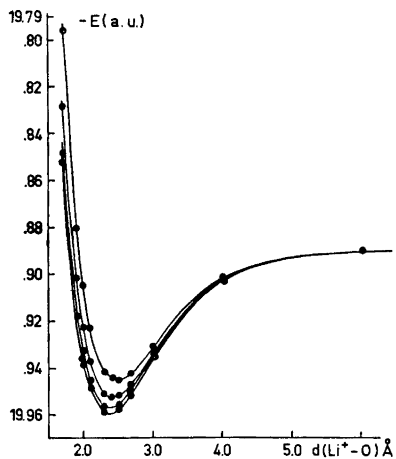


Fig. 2. Energy curves for the $d(\text{Li}^+-\text{O})$ variation of the systems $\text{Li}^+(\text{H}_2\text{O})_n$, $n=1, 2, 4, 6$.

so that the curves were adjusted to the same scale.

In Table 2 the first two columns are the calculated values for the energy of the water molecule and the Li^+ ion. In Table 2 the three last columns and the three columns of Table 3 are, respectively,

the total energies of the hydrated ion, the hydration energy, and the distance between the ion and the water-oxygen atom.

In the CNDO/2 calculations the total energies of H_2O , F^- , and Cl^- was found to be -19.88771 , -27.48407 , and -16.10429 a.u., respectively, and the total energies of Li^+ and Na^+ were taken to be zero.

Discussion. The basis set III in *ab initio* calculations is most closely related to the basis-set in CNDO/2 calculations. The ΔE 's for $\text{Li}^+(\text{H}_2\text{O})$ calculated by the CNDO/2 method and by basis set I agree very well, while ΔE for basis-set III is closer to the experimental value, which for $\text{Li}^+\text{H}_2\text{O}$ is -34 kcal/mol.¹⁴ ΔE seems to be very sensitive to the basis set.

For $\text{Li}^+(\text{H}_2\text{O})_2$, the ΔE 's from the *ab initio* and the CNDO/2 calculations are similar while the experimental value is -59.8 kcal/mol.¹⁴

The greatest difference in the CNDO/2 and *ab initio* results is in the equilibrium distances. For $\text{Li}^+\text{H}_2\text{O}$ and $\text{Li}^+(\text{H}_2\text{O})_2$ the difference in $R_{\text{Li-O}}$ is about 30%. Compared to the crystal structure determination ($R_{\text{Li-O}} = 1.939$ Å) for 4-coordination on Li,¹⁵ the *ab initio* calculations are closer to the experimental values than those obtained by the CNDO/2 method. Equilibrium distances do not seem to be greatly affected by the basis set as can be seen from Fig. 1.

1. Burton, R. E. and Daly, J. *Trans. Faraday Soc.* **66** (1970) 1281.
2. Burton, R. E. and Daly, J. *Trans. Faraday Soc.* **66** (1970) 2408.
3. Burton, R. E. and Daly, J. *Trans. Faraday Soc.* **67** (1971) 1219.
4. Lischka, H., Plesser, T. and Schuster, P. *Chem. Phys. Letters* **6** (1970) 263.
5. Diercksen, G. H. F. and Kraemer, W. P. *Chem. Phys. Letters* **5** (1970) 570.
6. Schuster, P. and Preuss, H. W. *Chem. Phys. Letters* **11** (1971) 35.
7. Diercksen, G. H. F. and Kraemer, W. P. *Theor. Chim. Acta* **23** (1972) 387.
8. Diercksen, G. H. F. and Kraemer, W. P. *Theor. Chim. Acta* **23** (1972) 393.
9. Clementi, E. *J. Chem. Phys.* **57** (1972) 1077.
10. Davies, D. R. and Clementi, E. QCPE 92, IBMOL.
11. Veillard, A, IBMOL: Computation of wavefunction for molecules of general geometry. Version 4, Special IBM Report 1968. Due to the small memory of our computer (an IBM 360/50 with 300 k bits available to the users) we had to modify these programs accordingly.
12. Quantum Chemistry Program Exchange (QCPE) No. 141, CNINDO, Chemistry Department, Indiana University, Bloomington, Indiana 47401, U.S.A.
13. Roos, B. and Siegbahn, P. *Theor. Chim. Acta* **17** (1970) 209.
14. Dridic, I. and Kebarle, P. *J. Phys. Chem.* **74** (1970) 1466.
15. Durant, P. F., Piret, P. and van Meerseche, M. *Acta Cryst.* **22** (1967) 52.

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KEMISK BIBLIOTEK

Den kgl. Veterinær- og Landbohøjskole