THEORETICAL INVESTIGATION
OF THE INTERACTION ENERGY
IN THE Li⁺ + H₂O IONIC COMPLEX*

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The interaction energy between the Li^+ ion and the water molecule has been studied at the ab initio SCF + MBPT(2) level in localized representation.

The result obtained for the SCF interaction energy calculated by basis set of moderate size shows that the counter-poise correction reduces this quantity by about 30 %.

The correlation energy contributions have been computed accordingly to the localized molecular orbitals (LMOs).

Some interesting results were obtained for the interpair-correlation energy quantities between the Li^+ and the LMOs of the H_2O molecule.

1. Introduction

It is well known that the supermolecular approach is adequate for the determination of the interaction energy of molecules. It is also agreed that in this method the calculated energy difference — at least at the Hartree–Fock level — must be corrected because of the basis set superposition error (BSSE). It is usually the so-called counter-poise method [1] which is applied for that purpose. As to the correlated level, on the other hand, it is doubted, whether the BSSE — which is inevitably to be taken into account for the calculation of the intermolecular energy — can be avoided in the same way. Several ideas have arisen and have been rationalized for the elimination of the BSSE at the correlated level in the past years. No general method has yet been elaborated, however, up to now for the solution of this problem.

It is evident that the investigation of as many as possible interactions could help to obtain much information in the above-mentioned field. The interaction energies between neutral molecules have already been investigated by several authors. The study of the interaction between (positive or negative) ions and other systems is less favoured. There are some works published in this field, of course, but the investigations are not as exhausting as for neutral monomers.

A restricted number of discussions — both from experimental as well as from theoretical aspects — are known for the interaction of alkali ions and the water

*Dedicated to Prof. R. Gáspár on his 70th birthday

molecule. Special attention was paid to studying the interaction energy between lithium ions and water.

An interesting work has been published already in 1980 [2] on the experimental properties of the lithium ions in aqueous solution. The hydration number and the orientation angle between the Li^+ ion and the water molecule has been investigated by the method of neutron diffraction. Several theoretical studies have been published and also ab initio calculations performed on the same subject [3–5]. Special basis sets, furthermore, have been proposed [6,7] for the study of the interaction energy of ionic complexes.

2. Method of calculations

The interaction between the Li^+ and the water molecule has been chosen as the subject of our calculations. The method is based on the use of localized molecular orbitals (LMOs) both at the Hartree–Fock as well as the correlated levels. The well-known Boys' localization procedure [8] has been applied for the determination of the LMOs. The calculations of the LMOs' contributions (at the Hartree–Fock level: Fock-matrix elements, first order electric moments etc. and at the correlated (MP2) level diagonal and off-diagonal pair-correlation energies) have been performed by the method elaborated in our Group in the past years [9–11].

The basis sets MINI and MIDI [12] were used in the actual calculations, which sets are known to give rise to small BSSEs. Two specific configurations have been investigated for the $Li^+ + H_2O$ complex and the values at these most attractive geometry arrangements were calculated at different intermolecular distances. The total energy quantities obtained at the HF as well as at the correlated levels are given in Table I. The results clearly show that

  a) the MIDI basis set is quite adequate for the study (at least as large a set is necessary for the calculation of the correlation energy), and
  b) the localized representation approximates correctly the canonical one at the MP2 level.

All of the calculations have been performed on IBM PC/AT compatible machines at the Technical University of Budapest.

3. Results obtained at the Hartree–Fock level

As mentioned above, the $H_2O + Li^+$ complex has been investigated by the method of neutron diffraction [2]. The results have shown that the Li^+ prefers its position near to the direction of the oxygen atom's lone pair (but not exactly!). The closest position between the Li^+ ion and the H_2O molecule is at an angle a bit smaller than that of the lone pair's charge distribution. The aim of our calculation is twofold:

  a) to present that the method proposed by us is useful also for the study of ionic complexes, and

Table I
Total energies obtained for the studied systems
(values given in Hartree)

Systems and Basis set	SCF energy	Correlation energy contributions in	
		canonical	localized
		representation	
Li atom MINI	−7.378092	−0.276210 − 4	−
Li$^+$ MINI	−7.182534	−0.388261 − 4	−
Li atom MIDI	−7.380800	−0.276210 − 4	−
Li$^+$ MIDI	−7.185210	−0.742262 − 4	−
H$_2$O MINI	−75.454960	−0.321606 − 1	−0.327351 − 1
H$_2$O MIDI	−75.493148	−0.119813	−0.119144 − 1
H$_2$O + Li$^+$ MINI			
$d = 3.0$ Bohr	−82.721774	−0.417004 − 1	−0.355491 − 1
$d = 3.5$ Bohr	−82.727459	−0.420981 − 1	−0.381632 − 1
H$_2$O + Li$^+$ MINI			
$d' = 3.0$ Bohr	−82.699007	−0.404726 − 1	−0.408797 − 1
$d' = 3.5$ Bohr	−82.710919	−0.417344 − 1	−0.421645 − 1
H$_2$O + Li$^+$ MIDI			
$d = 3.0$ Bohr	−82.754297	−0.121863	−0.121019
$d = 3.5$ Bohr	−82.760401	−0.122888	−0.121969
$d = 4.0$ Bohr	−82.750193	−0.123434	−0.122441
H$_2$O + Li$^+$ MIDI			
$d = 3.0$ Bohr	−82.733801	−0.122298	−0.122198
$d = 3.5$ Bohr	−82.746082	−0.123941	−0.123097
$d = 4.0$ Bohr	−82.739565	−0.124969	−0.124178

Note. In the Table d denotes the distance between the Li$^+$ ion and the O atom, respectively, in the cases when both nuclei lie on the z-axis. Similarly, d' denotes the corresponding distance when the Li$^+$ ion approaches from the direction of one of the oxygen atoms' lone pair LMO. The correlation energies are calculated at the MP2 level.

b) to study whether the localized representation is able to reflect the energetical differences in the intersystems energies due to the changes in the geometrical orientation.

Let us first look at the Fock-matrix elements. The values calculated both by MINI and MIDI basis sets are given in Table II, obtained at two specific geometrical arrangements. The "z-axis direction" means that the Li$^+$ is approaching from the opposite direction (but the same plane) where the two hydrogen atoms lie. The "sideways direction" means the approach of the Li$^+$ from the oxygen atoms' lone pair LMO. The results show (see Table II), that not only the localization of the canonical molecular orbitals can be performed for the studied ionic supermolecules,

Table II

Characterization of the localized orbitals in terms
of the Fock-matrix elements in the occupied space
for the H_2O + Li^+ systems (values are given in a.u.)

Basis set	No of orbitals	Direction: z-axis	
		$d = 3.0$ Bohr	$d = 3.5$ Bohr
MINI	1	-17.2429	-18.6992
	2	-4.2756	-2.7775
	3	-2.6651	-2.6809
	4	$-1.2142(2\times)$	$-1.1892(2\times)$
	5	-1.0007	-0.9681
MIDI	1	-20.6357	-20.6209
	2	-2.6591	-2.6807
	3	-1.4118	-1.3972
	4	-1.2461	-1.1900
	5	-0.9835	-0.9577
	6	-0.8079	-0.7814
		Direction: sideways	
MINI	1	-20.5047	-20.4993
	2	-2.6869	-2.7005
	3	-1.2926	-2.7005
	4	-1.1633	-1.0977
	5	-1.0463	-1.0341
	6	-0.9735	-0.9488
MIDI	1	-20.6460	-20.6324
	2	-2.6846	-2.7000
	3	-1.4228	-1.4067
	4	-1.2376	-1.1873
	5	-0.9917	-0.9665
	6	-0.8210	-0.7557

but the Fock-matrix elements in localized representation change systematically with
the changes of the geometrical parameters as well.

4. Results obtained at the correlated level

The total (MP2) correlation energy quantities were given in Table I. The pair-
correlation energies (which are in close connection with the interaction energy, see,
e.g. [10,11,13]) between the Li^+ core LMO and the LMOs of the H_2O molecule
are demonstrated in Table III. The values are tabulated at different intermolecular
distances (around the energetical minimum) for two geometrical arrangements. It is
interesting to note that the pair-correlation energies change systematically with the
changes of the intermolecular distance (i.e. there is a decrease in the values as the
Li^+ comes farther and farther from the H_2O molecule). No significant differences,
however, could be found — at first look — between the values calculated for the

Table III

Pair-correlation energy contributions of the
localized orbitals obtained for the H$_2$O + Li$^+$
system (in Hartree)

Basis set: MIDI	Directions	
Intermolecular distance	z-axis	sideways
3.0 Bohr Li$^+$/core of H$_2$O	−0.1080 − 5	−0.8895 − 6
Li$^+$/orb2 of H$_2$O	−0.2733 − 4	−0.3268 − 4
orb3	−0.5510 − 4	−0.4418 − 4
orb4	−0.4384 − 4	−0.2263 − 4
orb5	−0.3747 − 4	−0.3670 − 4
3.5 Bohr Li$^+$/core of H$_2$O	−0.3852 − 6	−0.2996 − 6
Li$^+$/orb2 of H$_2$O	−0.1507 − 4	−0.1077 − 4
orb3	−0.1961 − 4	−0.1489 − 4
orb4	−0.9909 − 5	−0.7394 − 5
erb5	−0.1264 − 4	−0.1217 − 4
4.0 Bohr Li$^+$/core of H$_2$O	−0.1250 − 6	−0.9681 − 7
Li$^+$/orb2 of H$_2$O	−0.5815 − 5	−0.4050 − 5
orb3	−0.6779 − 5	−0.5053 − 5
orb4	−0.3491 − 5	−0.2468 − 5
orb5	−0.3875 − 5	−0.4343 − 5

Note: Li$^+$/core, Li$^+$/orb2, etc. denote the interpair energy
contribution between the Li$^+$ and the core, that between
the Li$^+$ and the second LMO of the H$_2$O, etc.

directions "z-axis" and "sideways", respectively. The values obtained for the latter arrangement are usually slightly smaller than those obtained for the former orientation. It is remarkable, however, that at the intermolecular distance of 3.0 Bohr (a distance short enough for some of the LMOs being rather close to each other) pair-correlation energy between the core of the Li$^+$ and the LMO No. 3. of the H$_2$O is larger in the sideways arrangement than in the other geometrical one. The energy quantity is, namely, $-0.3268 \cdot 10^{-4}$ while all of the other quantities are smaller than the corresponding values obtained at the z-axis orientation.

It is important to emphasize that exactly this localized orbital No. 3 corresponds to that LMO which is oriented toward the Li$^+$. This result clearly shows that the localized representation is capable of reflecting suitably not only the intermolecular interactions in general, but the quantities decomposed into special contributions can help to shed light on some details of the intermolecular interactions as well.

References

1. S. F. Boys and F. Bernardi, Mol. Phys., *19*, 553, 1970.
2. J. R. Newsome, G. W. Neilson and J. E. Enderby, J. Phys. C. Solid St. Phys., *13*, L923, 1980.
3. H. Kistenmacher, H. Popkie and E. Clementi, J. Chem. Phys., *61*, 799, 1974.

4. J. B. Collins, P. V. R. Schleyer, J. S. Binkley, J. A. Pople and L. Radom, J. Am. Chem. Soc., 98, 3436, 1976.
5. J. Sauer and P. Hobža, Theoret. Chim. Acta (Berlin), 65, 291, 1984.
6. J. E. Del Bene, J. Comp. Chem., 7, 259, 1986.
7. R. Cammi, H. J. Hofmann and J. Tomasi: Theoret. Chim. Acta (Berlin), 76, 297, 1989.
8. S. F. Boys, in Quantum Theory of Atoms, Molecules and Solid State, P. P. Löwdin, Ed. Academic Press, New York, 1966.
9. E. Kapuy, Z. Csépes and C. Kozmutza, Int. J. Quant. Chem., 23, 981, 1983.
10. C. Kozmutza and E. Kapuy, Int. J. Quant. Chem., 38, 665, 1990.
11. E. Kapuy and C. Kozmutza, J. Chem. Phys., 94, 5565, 1991.
12. H. Tatewaki and S. Huzinaga, J. Compl. Chem., 1, 205, 1980.
13. C. Kozmutza and E. Kapuy, J. Comp. Chem., (to be published).