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A conceptual framework chemistry of Hydrated Cations: Part I. Preliminary *Ab Initio* and QTAIM calculations on $[Li(H_2O)_n]^+$ (n=1,2,3).

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ABSTRACT

Ion molecules with general chemical formula as $[Li(H_2O)_n]^+$ (n=1,2,3), have been chosen as model species to investigate the chemical properties of hydrated lithium cations. The RHF(SCVS)/UGBS level of calculation has been used for obtaining equilibrium geometries and Rho(r) functions (electron density distributions). By the aid of fundamental physical theorems implemented in Quantum Theory of Atoms in Molecules (QTAIM), the structures, the physical nature of chemical bonds and all atomic properties have been determined for cited species at the mentioned theoretical level. Then these atomic properties have been compared with their corresponding values in isolated Li^+ and H_2O ingredients. ***Fragments of a molecule, Interaction and Coordination*** are the three fundamental concepts in this field, which have been fully discussed and redefined unequivocally in a new context.

Keywords: Hydrated Li^+, QTAIM, Chemical Bond, Interaction, Coordination.

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INTRODUCTION

Aqueous solutions of solvated cations are the subject of broad investigations in both experimental and theoretical chemistry[1-8]. Among them, the cations of group IA conducted a large portion of activities in theoretical chemistry due to their vital role in biological systems[2-5,8]. From the time of Clementi's pioneering work[9] till now, lots of reports have been published considering the details of potential energy surfaces (PES) of $[Li(H_2O)_n]^+$. In this direction, in an interesting paper, Feller and coworkers[10] provided a complete computational search on PES of $[Li(H_2O)_n]^+$ species confining themselves to n=1-6. They mentioned that the lithium-water interaction is largely electrostatic in nature whereas, their discussion about the coordination number of Li^+ was based on classical approach, employing the Li-O internuclear distances. In another paper, Feller and Glendening[11] have reported a complete search on PES's of $[M(H_2O)_n]^+$ molecules in which, "M" was a member of Group IA elements whereas, "n" varies up to six. Not only the hydration energies and equilibrium geometries of cited clusters were reported, but also the special notation namely, "n+m" has been proposed for the coordination around central cation[11]. In this notation, "n" indicates the number of members of the primary shell namely, water molecules "directly" coordinating the metal cation and "m" gives the number of secondary shell denoting, the water molecules i.e those that are separated from cation by one intervening water molecule " . One of interesting aspects of this paper[11] is the assignment of classical frame (structure) to each cluster. On the other hand, the H-bonding patterns between neighboring O and H centers were also been proposed in larger size clusters[11]. To evaluate the polarizations, charge transfer and exchange repulsion or more precisely analyzing "interactions", Morokuma and coworkers adopted a partitioning scheme at the Hartree-Fock level[12-14]. In this accord, Glendening[15] proposed an alternative approach called, Natural Energy Decomposition Analysis (NEDA) based on NBO method. The two body interactions[16] that had been simulated by putative Lennard-Jones potential energy functions (parameters adopted according to ab initio data) were employed to model the interactions between central cation and water molecules. Microscopic solvation of neutral and cationic $Li(H_2O)_n$ (n=1-6 and 8) species[17] was also the subject of theoretical study of Hashimoto and Kamimoto. In line with other previous reports, they also asserted that the interior structure of cited clusters is composed of four H_2O molecules and more in the second shell. On the other hand, simulation methods like classical Monte Carlo and Car-Parrinello BLYP molecular dynamics confirmed that indeed the first shell around Li^+ is composed of four water molecules[18,19].

Recently, Tarakeshwar and coworkers [20] have reported the theoretical structures, energies and vibrations of monovalent cation-water clusters $M^+(H_2O)_{1-6}$ including Li^+ cation, at both MP2 and DFT levels. The discrepancy for evaluating the coordination number of cations was well addressed [20]. All of the various structures in their report have been assigned classically. They also reported the interaction energy components of the cation-water interactions.

Partitioning, Interaction and Coordination: revisited

A glance at the above history and technical details, reveals that some concepts in this field are ambiguous. In traditional notation , two parts of cation-water clusters are distinguishable: a cation and surrounded water molecule(s). Although, it is true that experimental observations indirectly confirm this notation, but one may pose the questions: "Does quantum mechanics directly confirms this picture?" Or more precisely: "Are cationic and aqueous species well defined quantum mechanical subsystems in these clusters?". This is in the heart of "partitioning" problem.

The other relevant concept is "interaction". Without any definite subsystems, it is impossible to consider the interactions precisely. The Murokoma's and NEDA approaches were the first efforts for effective partitioning schemes, but both of them had their own limitations. For instance, the first approach could only been applied at HF level whereas, the second methodology was constructed on "arbitrary based" NBO analyses. So, none of these and similar methods were unique (by the word unique we mean that a model independent methodology).

There are also ambiguities regarding the concept of "coordination". The internuclear distances between Li and O, can not serve as an exact measure of this concept especially in large cation-water (n= 5, 6, …) clusters where, there are broad range of internuclear distances and the clusters possess no special local symmetries (this is indeed a general problem for non-stereosymmetric molecules and clusters). As an example, one may imagine a situation where two O nuclei, lay 1.9 and 2.0 Å apart from Li nucleus so, do they belong to the same shell around Li or not? A definite threshold distance should be proposed in each cluster as the cutting edge between bonded and non-bonded interactions, but this threshold distance is not unique and so it is inevitably arbitrary defined (or at least based on a convention) and will be changed with the size of cluster or even one's decision. Therefore, the concept of coordination has remained ambiguous or at least fuzzy. So, it is clear (at least for whom interested in precision) that a methodology is needed to provide unequivocal answers to the above-mentioned questions. So, the fallowing sections of this paper have been devoted to possible answers for such questions in the context of Quantum Theory of Atoms in Molecules (hereafter abbreviated as QTAIM).

In the end of this section we also want to quote a warning (which seems serious according to our previous experiences). One must always keep in mind that the terminology employed in this paper is developed and then extracted within the context of QTAIM and the reader should not confuse them with similar terms, which have been used or currently in use within the context of classical chemistry. All such terms used in this paper have been discussed in detail or redefined carefully to avoid semantic confusions.

Computational Details

The restricted Hartree-Fock Self Consistent Virial Scaling method (RHF(SCVS))[21] with universal the basis set, UGBS(s,p) [22] has been used for geometry optimizations, frequency calculations and evaluation of Rho(r) functions of $[Li(H_2O)_{1-3}]^+$ ion-molecules. The SCVS method produces the HF wavefunctions that satisfy the Virial theorem exactly. According to our experiences, such calculations reduce integration errors in QTAIM calculations. The choice of method seems reasonable due to negligible effect of electron correlations on the geometries of these small clusters. The resulted energies and geometrical parameters were comparable with the near HF limit calculations employing cc-pVxZ hierarchal set. In spite of large number of uncontracted basis functions in this basis set, our experiences clearly demonstrate that using only the s and p type functions reduce the QTAIM integration errors much better rather than employing alternative contracted basis sets that contain d and f type functions. All ab initio quantum chemical calculations were performed using GAMESS6-4[23] suite of programs and the corresponding QTAIM calculations with MORPHY99 [24-29] and AIM2000[30-32] packages.

RESULTS AND DISCUSSION

Since this paper is based on QTAIM methodology, some relevant important points of this theory seems worth-mentioning although, a detailed discussion may be found elsewhere. By applying the Schwinger's principle of stationary action in quantum mechanics, Bader and coworkers have demonstrated that total electron density of molecule (Rho(r)) is divided to 3D parts with well-defined borders[33,34]. All these parts or fragments, obey the laws of quantum mechanics and the sum of their properties (the expectation values of hermitian operators) produce the corresponding molecular values[34]. In brief, the theory of open quantum systems allows the division of molecule (as a system) to its fragments (as subsystems) uniquely. Therefore, this partitioning scheme does not depend on how the Schrödinger equation is solved (it is “method” independent)[34]. In comparison to known experimental facts, Bader proposed these fragments as the “chemical atoms” and the theory was called “Quantum Theory of Atoms in Molecules” [35](On must keep in mind that QTAIM is a special version (relevant in theoretical chemistry) of general theory of open quantum subsystems[34]). As mentioned previously, the details of the theory have been well documented elsewhere[33,36,37] so, we just describe the results of application throughout this paper. To start the QTAIM analysis, a brief survey on general qualitative topological characteristics of charge densities of species under study has been accomplished and then the atomic expectation values will be discussed.

The gradient vector fields (GRVF) [36] and contour maps of charge density of $[Li(H_2O)_{1-3}]^+$ clusters have been depicted in Fig 1(a,c,e) and show how each one has been divided to well defined fragments. The 3D space of each fragment (chemical atom) which is confined by its border(s) (or inter-atomic surfaces[34]) is called “atomic basin”[36]. These are also depicted in Fig 1(b,d,f) for Li atom. As is evident from this figure, the QTAIM derived shapes of Li basins are completely different with each other in different ion-molecules. By integrating the properties over each atomic basin, the atomic properties have been calculated and gathered in table 1. The small differences between ab initio and integrated QTAIM make us confident regarding the reliability of employed numerical procedures and so allow the comparison of desired atomic properties within different clusters.

In each cluster, the Li basin bears almost ~1.0 (a.u.) positive charge, which diminishes smoothly from $[Li(H_2O)_1]^+$ to $[Li(H_2O)_3]^+$ ion-molecule. On the other hand, all O basins bear substantial negative charges (more than 1.0 (a.u) and about ~1.3 (a.u.)). The negative charge of each O basin is also reduced as the size of cluster increased. Interestingly, the net positive charge of each H basin is comparable to that of Li in each cluster (only ~0.3 (a.u.) smaller), and is also diminished with increasing the size of ion-molecules. Briefly, as the size of ion-molecule increases, more negative charge is transferred from negative basins (O basins) to positive basins (H and Li). So by size enlargement, charge separation decreases in ion-molecule series.

Regarding the calculated energies of atomic basins, the oxygen basin includes the major portion of total molecular energy in all cases. As is evident form table 1, by increasing the cluster size this contribution is reduced. The opposite behavior is seen for energies of Li and H basins. It is interesting to note that with combination of these data with those discussed in previous paragraph, one may find a clear correlation between direction of charge transfer and energies calculated for each basin. In all cases studied, the energy of a portion decreases with the inward flow of electronic charge whereas the energies increase with outward flow of electronic charge. On the other hand, one must keep in mind that the 3D energy partitioning enables us also to compare the total energies of atomic basins to some reference points. These choices may be selected as the isolated H_2O and Li^+ ingredients. In spite of similar atomic properties of O, H and Li atomic basins of each cluster to that of H_2O and Li^+ (table 1), we will provide more direct arguments for selecting them as references and leave the comparison to the last part of the paper.

The changing pattern of atomic volumes[38] is also worth mentioning. In each cluster one may found: V(O) > V(Li) > V(H). On the other hand, by increasing the size of cluster the atomic volumes of O and H atoms grow slightly whereas, the volume of Li atom decreases. The other interesting point that can be driven from table 1 and figure 1 is the magnitude of inter-atomic electric dipole moment (Q) which is one of characteristics of detailed pattern of charge distribution in an atomic basin. Although the Li basin is not spherical, but in each clusters it has a zero (or nearly zero) electric dipole moment. The values of Q for H and O atomic basins are in the same order within each cluster. The difference between the values of Q for O and H atomic basins is 0.0106, 0.0160 and 0.0370 (a.u.) going from $[Li(H_2O)_1]^+$ to $[Li(H_2O)_3]^+$, respectively. If the value of Q is assumed as the degree of charge polarization (but not deformation) in atomic basins (or at least one of important relevant quantities), table 1 demonstrates that not only O basin(s) undergo(s) the largest polarization in each molecule, but also the rate of polarization change within this basin is greater than that of Li and H basins through the studied clusters.

Interaction, Structure and Path of nteraction

With the fragments in hand, it is now possible to investigate the interactions. This concept can be defined via topological behavior of gradient vector field of charge density[36]. As figure 1 (a,c,e) demonstrates, if two atoms share common border(s), they have interaction(s) with each other. This is a natural consequence of partitioning theorem[34]. In some cases like figure 1 (a) the map is clear enough to distinguish the interactions but in complicated cases like Fig 1(c,e) this is not an easy task.

According to QTAIM, the interacting atoms (atomic basin) or more precisely the "bonded atoms", have been determined by two Gradient Paths (GPs)[36,39] of charge density function, which originate from a bond critical point (BCP)[36], a point where gradient of charge density vanishes and the Hessian matrix of charge density has two negative and one positive eigenvalues, and terminated at neighboring nuclei [39]. These GPs at equilibrium geometry are called bond paths (BPs)[39] (Molecular geometry is the list of nuclei 3D coordinations[36]). The presence of BPs is the necessary and sufficient condition for two atoms so linked, to be bonded to one another[39]. The BCPs and their associated BPs construct the quantum mechanical structure of molecule, which is known as molecular graph (MG)[36]. The MG of each ion-molecule has been depicted in Fig 2. As Fig 2 shows rigorously, in all cases the Li atom has only interaction with O atom(s) and each of O atoms with only two H atoms. Therefore, the structure naturally determines the interactions.

Now it is the time of determining the direction(s) of interactions. Figure 1 (b,d,f) show that each atom is a 3D topological "object" in real space[35,36]. These atoms interact with each other via their border(s) or inter-atomic surfaces (IASs). The general structural homeomorphism[40] observed between the electron density and the virial field[35] demonstrates that "every BP is mirrored by corresponding virial path (a line linking the same neighboring nuclei along which the potential energy density is maximally negative i.e. maximally stabilizing with respect to any neighboring line)"[39]. The presence of such homeomorphism underlies the energy lowering and makes BP the **universal indicator of bonded interactions**[39]. Therefore QTAIM theorems provide definite paths of interaction through 3D space. Ultimately, MG not only shows the quantum mechanical structure of molecule, but also shows the preferred path of interaction between QTAIM atoms (chemical atoms).

Molecular Graph versus Classical Frame of Molecule

This short paragraph has been spent to compare the MG (extract from topological characteristics of charge density distribution) with Classical frame of molecule, which only connects the neighboring nuclei by a straight line (usually relies on internuclear distances). This comparison is usually performed by taking into account the internuclear distances (IDs) and associated length of corresponding BPs. These data have been gathered in Table 2. According to this table, BPs' lengths and IDs are virtually the same. The corresponding values for OH bonded interaction in an isolated H_2O have been also presented for comparison.

Bonding Scheme

The major classification of bonded interactions[36,37] in the framework of QTAIM has been proposed based on the sign of Laplacian of electron density ($\nabla^2\rho_b$) at BCP. Shared interactions are characterized with a $\nabla^2\rho_b<0$ and Closed shell interactions with $\nabla^2\rho_b>0$. The complete list of critical points of electron density (where $\nabla\rho=0$) and their mathematical characters have been gathered in table 3 for each of species considered. The completeness of CP analysis has been checked by satisfaction of Poincare-Hopf rule[36] in each case.

According to table 3, in all cases closed shell interactions exist between Li and O atoms and shared interactions between each O and two H atoms. The mathematical characteristics of BCPs of O and H atoms bonded interactions in isolated water molecule at the same level of calculation are comparable to that of O and H atoms bonded interactions in ion-molecules (the same order of ρ_b, $\nabla^2\rho_b$, ε). On the basis of the amount of atomic charges and the values of ρ_b both closed shell and shared interactions may be divided to subgroups[36]. In attention to Gillespie-Popelier discussion[37], table 1 and table 3, represent the following bondings natures: all Li-O bonded interactions are closed shell and predominantly ionic ($\nabla^2\rho_b>0$, large atomic charges and ρ_b order of 10^{-2} a.u.) whereas, all O-H bonded interactions are shared polar covalent ($\nabla^2\rho_b<0$, different atomic charges and ρ_b order of 10^{-1} a.u.).

It should be mentioned here that the atomic charges themselves could not give the correct picture of bonded interactions. Both H and Li atoms have substantially positive atomic charges (table 1) therefore the nature of both Li-O and H-O bonded interactions could be regarded (wrongly!) as electrostatic. This is the Laplacian of electron density that reveals the difference between the natures of bonded interactions.

Coordination

The answer to this question is straightforward in the context of QTAIM. The full discussion has been done elsewhere for more complicated cases[41]. Natural definition of coordination number has been proposed based on topological analysis of charge density distribution. Accordingly, the coordination number of a certain atom in a molecule is the number of atoms in molecule that are connected (in a stable topological MG) by one or more (this is a rare situation) BPs to that certain atom[41].

According to Fig 2, all species posses stable MGs therefore, coordination number of Li atom in $[Li(H_2O)]^+$ is one, two in $[Li(H_2O)_2]^+$ and three in $[Li(H_2O)_3]^+$ ion-molecule. This definition is well applicable to other clusters of various sizes and complexity without any conceptual discontinuity.

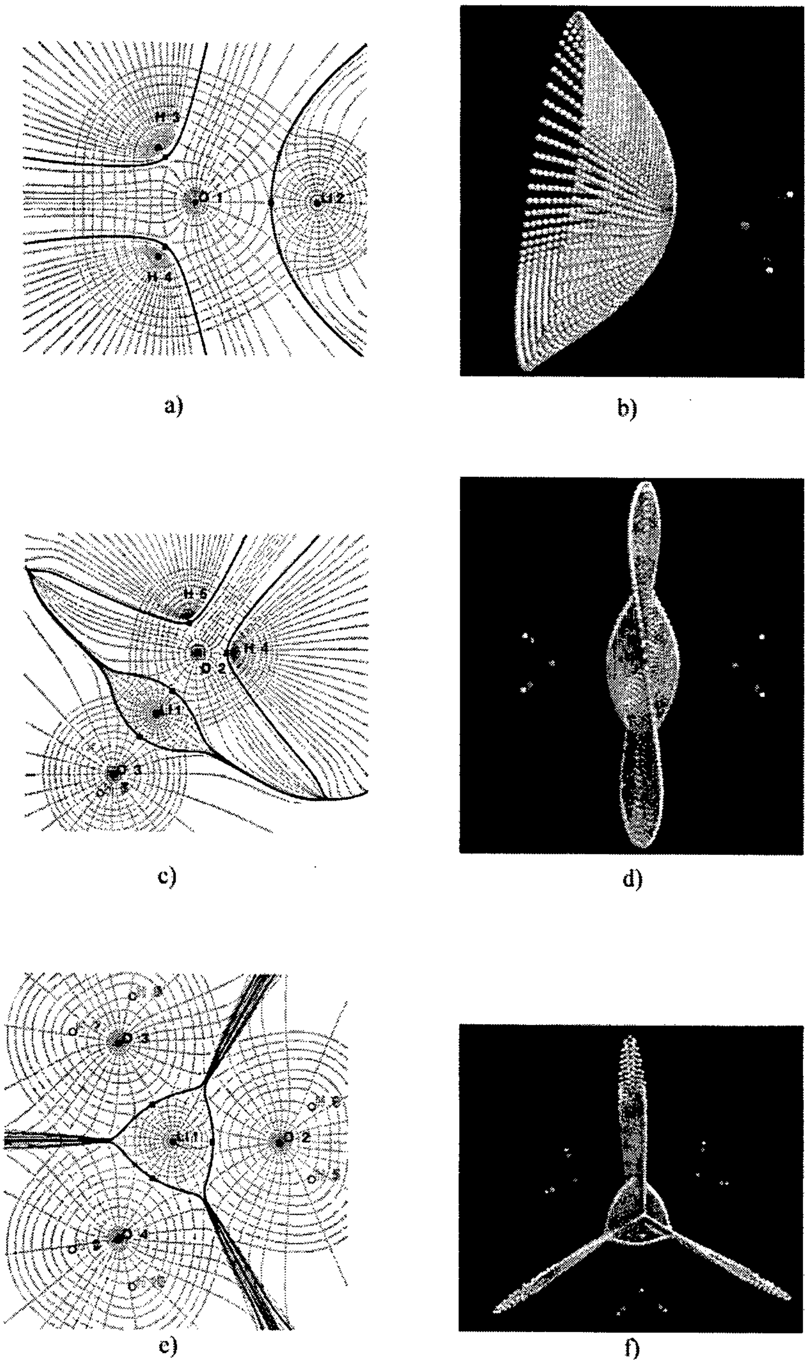
Conclusion

The three key concepts called: Fragments, Interaction and Coordination have been rigorously defined on the basis of fundamental partitioning theorems implemented in Quantum Theory of Atoms in Molecules and well applied to investigate some of the chemical properties of $[Li(H_2O)_{1-3}]^+$ clusters.

Atomic properties, molecular graphs and mathematical characteristics of critical points of Rho(r) function confirm that each cluster is composed of a cationic part (Li basin) and corresponding aqueous part(s), the former bonded via predominantly ionic bonded interactions to O atom(s) of aqueous part(s). The majority of positive charge has been accumulated in cationic part therefore, the symbolic formula of these clusters as $[M(H_2O)_n]^+$ or $[M^+(H_2O)_n]$ will be acceptable, but it should be mentioned that the generality of this notation must be checked for larger clusters via the same analysis.

We back to our previous discussion about reference species. The choice of isolated Li^+ and H_2O is now well understood. By taking the atomic properties of O, H and Li^+ in these species as reference points (table 1), the relative energies of O, H and Li atomic basins of each ion-molecule were calculated (Li atomic basin relative to Li^+, O atomic basins relative to O atomic basin in H_2O and H atomic basins relative to H atomic basins in H_2O) and gathered in Table 4. According to this table, the formation of each cluster stabilizes the O and Li atoms whereas, destabilizes the H atoms. The interesting point is that the O atom becomes approximately twice more stable than Li in $[Li(H_2O)]^+$ but the energetic stabilities become almost the same in $[Li(H_2O)_2]^+$ and then reversed in $[Li(H_2O)_3]^+$. It sounds that cationic Li becomes more stable when became more hydrated (in line with energies offered in table 1) whereas, with the enlargement of clusters the O and H atoms seems to tend toward the energetic values of O and H basins in isolated H_2O molecule.

The homeomorphism between virial field and electron density underlies the existence of preferred direction of interactions between 3D atoms in real space including both ionic and van der waals interactions[42]. These directions were depicted via BPs in MG, which constructs the quantum mechanical structure of molecule. It is the molecular graph, which shows the topological behavior of charge density and ultimately has been employed to rigorously define the concept of coordination[41].

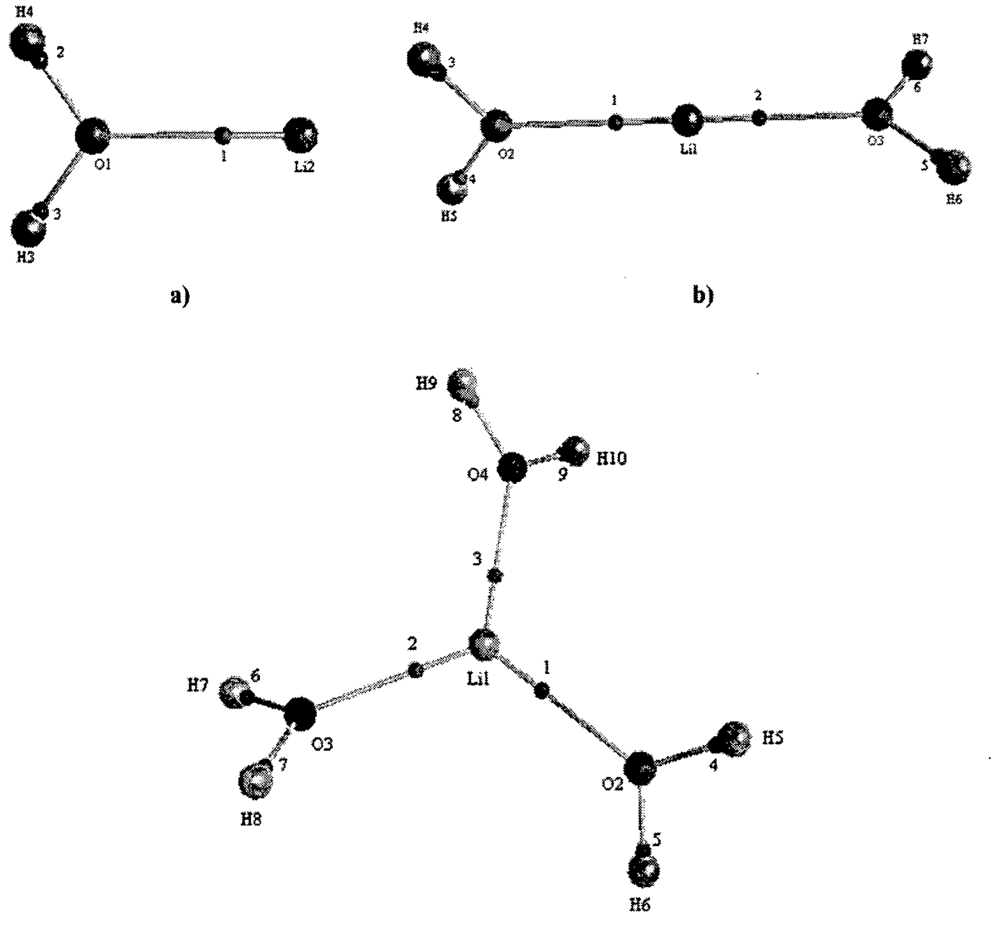


a) b)

c) d)

e) f)

Fig 1. Gradient vector fields & contour maps of charge density distributions: (GRVF) (a,c,e) and 3D atomic basins (b,d,f). **a)** GRVF map of $[Li(H_2O)]^+$, filled black curved lines are the intersections of inter-atomic surfaces (IAS) with plane of picture. **b)** 3D atomic basin of Li in $[Li(H_2O)]^+$. **c)** GRVF map of $[Li(H_2O)_2]^+$. **d)** 3D atomic basin of Li in $[Li(H_2O)_2]^+$. **e)** GRVF map of $[Li(H_2O)_3]^+$, hollow circles are out of plane nuclei. **f)** 3D atomic basin of Li in $[Li(H_2O)_3]^+$.



a) b)

c)

Fig 2. The 3D molecular graphs (MGs) of the equilibrium geometries at RHF(SCVS)/UGBS level of calculations. **a)** $[Li(H_2O)]^+$. **b)** $[Li(H_2O)_2]^+$. **c)** $[Li(H_2O)_3]^+$. Small Circles are BCPs.

Table 1. Atomic properties (offered in atomic units) from QTAIM analysis at RHF(SCVS)/UGBS level.

	Vol|0.001|[†]	q[‡]	E(Ω)[**]	L(Ω)[#]	Q[¶]	V/T
$\|Li(H_2O)\|^+$ (C_{2v})						
O1	136.57	-1.3010362	-75.423946	0.27E-03[##]	0.1334	
Li2	25.55	0.96690349	-7.2908134	-0.49E-04	0.0011	
H3	16.36	0.66719747	-0.31971658	0.42E-04	0.1228	
H4	16.36	0.66719729	-0.31971582	0.41E-04	0.1228	
Total	**194.84**	**1.00026205**	**-83.3541918**			
Total(ab initio)		**1.00000000**	**-83.3541025**			2.00000001
Δ *(AIM-Ab initio)*		**0.00026205**	**-0.0000893**			
$\|Li(H_2O)_2\|^+$ (D_{2d})						
Li1	25.67	0.94207297	-7.3330360	-0.77E-05	0.0000	
O2	136.81	-1.2880970	-75.413574	0.25E-04	0.1425	
O3	136.75	-1.2881050	-75.413571	0.19E-04	0.1425	
H4	16.80	0.65855706	-0.32580786	0.42E-04	0.1265	
H5	16.80	0.65855767	-0.32580749	0.42E-04	0.1265	
H6	16.81	0.65855758	-0.32580762	0.42E-04	0.1265	
H7	16.81	0.65855718	-0.32580777	0.42E-04	0.1265	
Total	**366.45**	**1.00010046**	**-159.4634117**			
Total(ab initio)		**1.00000000**	**-159.4632900**			2.00000001
Δ *(AIM-Ab initio)*		**0.00010046**	**-0.0001217**			
$\|Li(H_2O)_3\|^+$ (D_3)						
Li1	23.56	0.92860366	-7.3506396	-0.66E-04	0.0001	
O2	137.75	-1.2714333	-75.402843	0.29E-04	0.1680	
O3	137.75	-1.2714332	-75.402839	0.27E-04	0.1680	
O4	137.77	-1.2714345	-75.402838	0.26E-04	0.1680	
H5	17.37	0.64763986	-0.33346025	0.40E-04	0.1310	
H6	17.38	0.64764000	-0.33346018	0.40E-04	0.1310	
H7	17.38	0.64763878	-0.33346096	0.40E-04	0.1310	
H8	17.38	0.64763919	-0.33346092	0.40E-04	0.1310	
H9	17.37	0.64763889	-0.33346090	0.40E-04	0.1310	
H10	17.38	0.64763917	-0.33346092	0.40E-04	0.1310	
Total	**541.09**	**1.00013855**	**-235.5599237**			
Total(ab initio)		**1.00000000**	**-235.5597805**			2.00000002
Δ *(AIM-Ab initio)*		**0.00013855**	**-0.0001432**			
H_2O						
O1	142.86	-1.1784844729	-75.315153129	0.40E-04	0.2062	
H2	20.78	0.58924264405	-0.37113476220	0.77E-05	0.1582	
H3	20.77	0.58921428352	-0.37115651809	0.92E-05	0.1582	
Total	**184.41**	**-0.0000275453**	**-76.05744441**			
Total(ab initio)		**0.0000000000**	**-76.05736459**			1.99999998
Δ *(AIM-Ab initio)*		**-0.0000275453**	**-0.00007982**			
Li^+					0.0000	
Total(ab initio)			**-7.23641515**			2.00000000

[†] The atomic volume is integrated over atomic basin (Ω) to the contour surface of 0.001 a.u.

[‡] The total atomic charge.

[**] The total atomic energy that is calculated by integrating over atomic basin (Ω).

[#] The measure of total integration error over each atomic basin (Ω).

[¶] The total intra-atomic dipole moment.

[##] E-0n = 10^{-n}

Table 2 Comparison of bond paths length (BPL) and Internuclear Distances (ID) at RHF(SCVS)/UGBS level.

	Bonded Atoms	ID (Å)	BPL (Å)	Δ(ID-BPL)
$[Li(H_2O)]^+$ (C_{2v})				
	Li2-O1	1.817	1.817	0.000
	O1-H3	0.946	0.946	0.000
	O1-H4	0.946	0.946	0.000
$[Li(H_2O)_2]^+$ (D_{2d})				
	Li1-O2	1.848	1.848	0.000
	Li1-O3	1.848	1.848	0.000
	O2-H4	0.945	0.945	0.000
	O2-H5	0.945	0.945	0.000
	O3-H6	0.945	0.945	0.000
	O3-H7	0.945	0.945	0.000
$[Li(H_2O)_3]^+$ (D_3)				
	Li1-O2	1.887	1.887	0.000
	Li1-O3	1.887	1.887	0.000
	Li1-O4	1.887	1.887	0.000
	O2-H5	0.944	0.944	0.000
	O2-H6	0.944	0.944	0.000
	O3-H7	0.944	0.944	0.000
	O3-H8	0.944	0.944	0.000
	O4-H9	0.944	0.944	0.000
	O4-H10	0.944	0.944	0.000
(H_2O)				
	O1-H2	0.940	0.940	0.000
	O1-H3	0.940	0.940	0.000

Table 3 Mathematical Characters of CPs of the Rho(r) function at RHF(SCVS)/UGBS level.

	CP's number	Type of CP	ρ_b	$\nabla^2\rho_b$	ε	Connected Atoms
$[Li(H_2O)]^+$ (C_{2v})						
	1	BCP	0.04	0.32	0.08	Li2-O1
	2	BCP	0.38	-3.14	0.02	O1-H3
	3	BCP	0.38	-3.14	0.02	O1-H4
$[Li(H_2O)_2]^+$ (D_{2d})						
	1	BCP	0.04	0.29	0.08	Li1-O2
	2	BCP	0.04	0.29	0.08	Li1-O3
	3	BCP	0.39	-3.12	0.02	O2-H4
	4	BCP	0.39	-3.12	0.02	O2-H5
	5	BCP	0.39	-3.12	0.02	O3-H6
	6	BCP	0.39	-3.12	0.02	O3-H7
$[Li(H_2O)_3]^+$ (D_3)						
	1	BCP	0.03	0.26	0.08	Li1-O2
	2	BCP	0.03	0.26	0.08	Li1-O3
	3	BCP	0.03	0.26	0.08	Li1-O4
	4	BCP	0.39	-3.10	0.02	O2-H5
	5	BCP	0.39	-3.10	0.02	O2-H6
	6	BCP	0.39	-3.10	0.02	O3-H7
	7	BCP	0.39	-3.10	0.02	O3-H8
	8	BCP	0.39	-3.10	0.02	O4-H9
	9	BCP	0.39	-3.10	0.02	O4-H10
(H_2O)						
	1	BCP	0.40	-2.93	0.02	O1-H2
	2	BCP	0.40	-2.93	0.02	O1-H3

Table 4- Relative energies of QTAIM atoms at RHF(SCVS)/UGBS level.

	$E_r(\Omega)^{**}$ hartree	$E_r(\Omega)$ kcal/mol
Li^+	0.0000	0.0000
H_2O		
O1	0.0000	0.0000
H2 [#]	0.0000	0.0000
H3 [#]	0.0000	0.0000
$[Li(H_2O)]^+$ (C_{2v})		
O1	-0.1088	-68.27
Li2	-0.0544	-34.14
H3	0.0514	32.27
H4	0.0514	32.27
$[Li(H_2O)_2]^+$ (D_{2d})		
Li1	-0.0966	-60.63
O2	-0.0984	-61.76
O3	-0.0984	-61.76
H4	0.0453	28.45
H5	0.0453	28.45
H6	0.0453	28.45
H7	0.0453	28.45
$[Li(H_2O)_3]^+$ (D_3)		
Li1	-0.1142	-71.68
O2	-0.0877	-55.03
O3	-0.0877	-55.02
O4	-0.0877	-55.02
H5	0.0377	23.65
H6	0.0377	23.65
H7	0.0377	23.65
H8	0.0377	23.65
H9	0.0377	23.63
H10	0.0377	23.63

[**] Relative atomic energies have been calculated using the atomic energy of isolated Li^+ and the energies of O and H atoms in water molecule as references.

[#] The average atomic energy of H2 and H3 (-0.37115 hartree) has been used as a reference.

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