Study of the structure of molecular complexes. IX. The Hartree–Fock energy surface for the H_2O–Li–F complex*

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A large number of geometrical configurations (250) are computed with a large Gaussian basis set in the Hartree–Fock approximation for the H_2O–Li–F complex. The many-dimensional potential energy surface has been sampled by keeping the molecule of water at a fixed position and by allowing the lithium and the fluorine to assume many positions in space. Because of the symmetry (C_{2v}) of the water molecule, the 250 computations correspond to a sampling of about 600 configurations. The sampling includes a few highly repulsive configurations (up to about 300 kcal/mole in repulsion); the remaining points are either in the strongly attractive regions or in the weakly attractive regions of the surface. The stabilization energy of the complex reveals the existence of at least three possible structures: the Li–F–H_2O structure (with C_{2v} symmetry), with a stabilization energy (relative to H_2O, F^-, and Li^+) of about -186 kcal/mole; a second Li–F–H_2O structure with the fluorine forming a hydrogen bond (with one of the H–O groups of the water molecule), with a stabilization energy of about -191 kcal/mole; and a third structure, H_2O–Li–F (with C_{2v} symmetry), with a stabilization energy of about -201 kcal/mole. The main goal of this work is not the determination of the structures of the H_2O–Li–F complex, but the construction of a reliable potential to be used in the study of the structure and properties of ionic solutions. For this reason, the computed Hartree–Fock energies have been accurately fitted with a simple analytical expression. In addition, the Hartree–Fock energy for the complex has been analyzed by partitioning it into two-body interaction energies (Li–F, Li^+–H_2O, and F^-–H_2O) and into three-body potential-energy terms. Finally, a second type of partitioning, the so-called bond energy analysis, has been presented and discussed.

I. INTRODUCTION

We have previously considered a rather extended number of geometrical configurations, using the Hartree–Fock technique, and Gaussian basis functions for the Li^+–H_2O complex,[1] for the Na^+–H_2O and K^+–H_2O complexes,[2] for the F^-–H_2O and Cl^-–H_2O complexes,[3] for the H_2O–H_2O complex,[4] and for the Li^+–H_2O–H_2O complex.[5] The computed Hartree–Fock energies are chosen to sample the space of the potential surface from the repulsive region to the dissociation limits. To construct the *entire* surface, however, one needs a *continuous function* representing the surface; such a function was obtained for each of the above systems by fitting the computed Hartree–Fock energies with some analytical expression that was (a) accurate (say within 0.001 a.u. from the computed Hartree–Fock energies), and (b) simple, so as to be of use in cluster studies and in statistical mechanics where the interaction potential is the needed starting point.

In this work, we consider the H_2O–Li–F complex. The choice of this complex was motivated by a number of considerations. Firstly, since we wish to use the potential function derived here as the starting point in a study of ionic solutions, it is essential to consider a cluster having a water molecule in interaction with both a positive and negative ion. Up until now,[1–3,5] only anion–water or cation–water clusters were considered, or water alone was studied.[4] Secondly, and pursuant to the previous remark, we wish to consider an example that can be compared with earlier studies wherein a cluster of a single ion and a single water molecule was analyzed. Thirdly, we wish to study the importance of the three-body correction term, i.e., to study the reliability of the pairwise additivity assumption in the Hartree–Fock framework. The two-body Hartree–Fock potential has been applied to the study of liquid water,[4,7] small clusters of water,[8] and small clusters of water molecules containing a single ion.[9] A number of questions arise in such studies; for example, what is the importance of the correlation-energy correction to the two-body Hartree–Fock potential (esepcially for the water–water system), and what is the magnitude of the Hartree–Fock three-body corrections? In this paper, we shall not consider correlation-energy effects, but rather we will focus our attention on three-body effects determined using the Hartree–Fock model. Lastly, it is hoped that a study of the potential energy surface of the H_2O–Li–F complex may provide the kind of detailed information needed to initiate a study of the dielectric properties of aqueous solutions of electrolytes—starting from a somewhat more rigorous quantum-mechanical basis than has previously been available.[6]

Because this paper presents the first detailed results for a system of "three bodies" (Li^+, F^-, and H_2O), some discussion of the energy analysis for such a system is in order. Two analyses can be made. The first is the classically-motivated, pairwise additivity analysis which relates the total three-body interaction to a sum of two-body interaction terms, with a residual "three-body effect." The second procedure uses the quantum-mechanical bond energy analysis scheme (hereafter referred to as BEA), formulated sometime ago by one of us[10]; in this scheme, the total Hartree–Fock energy is partitioned into one-body, two-body, and three-body terms. Both analyses will be discussed and compared, and, in particular, we shall establish a direct relation-

ship between the classical decomposition and the quantum-mechanical BEA.

To fix our ideas, suppose we denote the total energy of the three-body system as $V(1, 2, 3)$ and the energy of the ith isolated one-body system as $V(i)$; then, we define the total stabilization energy in the usual way as

$$E(s, \text{ tot}) = V(1, 2, 3) - \sum_i V(i) . \quad (1)$$

Note that this energy is negative for a three-body complex which is more stable (lower in energy) than its isolated constituents.

A common assumption in many-body theory is the pairwise additivity assumption; here, the interaction energy of a three-body system is represented as the sum of two-body interactions. In terms of the stabilization energy, the assumption of pairwise additivity can be expressed formally as

$$E(s, 2) = \sum_{i<j} V(2, ij) . \quad (2)$$

Here, $E(s, 2)$ is a "two-body stabilization energy,"

$$V(2, ij) = V(ij) - V(i) - V(j)$$

is the stabilization energy of the isolated pair ij, and $V(ij)$ is the total energy of the isolated pair ij. In general, $E(s, 2)$ need not be the same as the total stabilization energy of the three-body system; accordingly, we may define a three-body stabilization energy,

$$E(s, 3) = E(s, \text{ tot}) - E(s, 2) . \quad (3)$$

The energy difference $E(s, 3)$ defines the classical, nonadditive contribution to the total stabilization energy of the system.

In the BEA, the total energy is decomposed into one-body, two-body, and three-body terms as follows:

$$V(1, 2, 3) = \sum_i \mathcal{E}(i) + \sum_{i<j} \mathcal{E}(ij) + \mathcal{E}(ijk) , \quad (4)$$

with the $\mathcal{E}(i)$, $\mathcal{E}(ij)$, and $\mathcal{E}(ijk)$ defined as in Ref. 10. This alternate, formally exact representation for the total energy of the three-body system can be interpreted physically in an appealing way. Let

$$P(i) = \mathcal{E}(i) - V(i) \quad (5a)$$

and

$$P(ij) = \mathcal{E}(ij) - V(2, ij) \quad (5b)$$

define the apparent perturbation to the isolated one-body and two-body energies, respectively, when the one-body and two-body systems are assumed present in a three-body cluster. Solving Eqs. (5) for $\mathcal{E}(i)$ and $\mathcal{E}(ij)$, substituting these into Eq. (4), and then using the resulting $V(1, 2, 3)$ in Eqs. (1)–(3), leads directly to the following expression for the three-body stabilization energy,

$$E(s, 3) = \sum_i P(i) + \sum_{i<j} P(ij) + \mathcal{E}(ijk) . \quad (6)$$

This result, based on BEA, provides an operational scheme for the analysis of the pairwise additivity approximation for a three-body system. In later sections of this paper, we shall use this scheme to analyze our numerical results.

II. CONFIGURATION SAMPLING

The Hartree–Fock energies have been obtained using a modified version of an existing computer program[11] (IBMOL—Version V) wherein molecular orbitals are expanded in terms of Gaussian-type contracted functions.[12] The orbital exponents and the contraction coefficients used in the calculations on the H_2O–Li–F complex are given in the Appendix of this paper (Tables A-1, A-2 and A-3). With this basis set, the Li–F potential curve was computed, and the data are reported in Table I. The Li–F distances R(Li–F) as well as the total energy are given in a.u. For comparison, we note that a very large basis set of Slater-type functions[13] yields a total energy of -106.9916 a.u. at R(Li–F) = 2.9877 a.u., a number which is to be compared with our value of -106.9845 a.u. As is known, a good fraction of this difference is in the poorer representation of the inner-shell $1s$ orbitals forced on the Gaussian set by lack of a proper cusp in the vicinity of the nucleus.

The total energy data of Table I have been fitted by the expression

$$E(\text{Li–F}) = \sum_{i=1}^{5} \frac{a_i}{R(\text{Li–F})^i} + a_6 \exp\left(\frac{a_7}{R(\text{Li–F})}\right) ,$$

where $a_1 = 183.747778$, $a_2 = 161.30035$, $a_3 = 79.10586$, $a_4 = 80.43912$, $a_5 = -7.56712$, $a_6 = -106.69458$, and $a_7 = 1.73191$. The standard deviation of the points given in Table I and of the data reported later in this paper for Li–F is 0.00004297 a.u.

TABLE I. Hartree–Fock potential for the LiF molecule (in a.u.).

$R_{(\text{Li–F})}$	Total energy	$R_{(\text{Li–F})}$	Total energy
1.50	−105.99874	8.0878	−106.81943
1.75	−106.49995	8.3106	−106.81597
2.00	−106.76368	8.73	−106.80998
2.35	−106.92416	9.00	−106.80643
2.45	−106.94762	9.0979	−106.80520
2.65	−106.97343	9.85	−106.79659
2.7877	−106.98151	10.3459	−106.79162
2.8877	−106.98405	10.6066	−106.78920
2.9877[a]	−106.98451	11.0522	−106.78534
3.20	−106.98074	11.0800	−106.78511
3.55	−106.96691	11.7216	−106.78010
3.6421	−106.96293	11.9279	−106.77861
3.920	−106.94900	12.00	−106.77810
4.50	−106.92065	12.65	−106.77377
5.00	−106.89913	13.8582	−106.76682
5.3055	−106.88753	15.00	−106.76130
5.5763	−106.87809	15.8595	−106.75767
5.7403	−106.87276	16.7705	−106.75423
6.0832	−106.86244	18.9940	−106.74724
6.2721	−106.85720	20.9845	−106.74224
6.58	−106.84930	20.15	−106.74422
7.00	−106.83964	22.50	−106.73903
7.50	−106.82958	30.0	−106.72792
		∞	−106.69458

[a]Equilibrium separation.

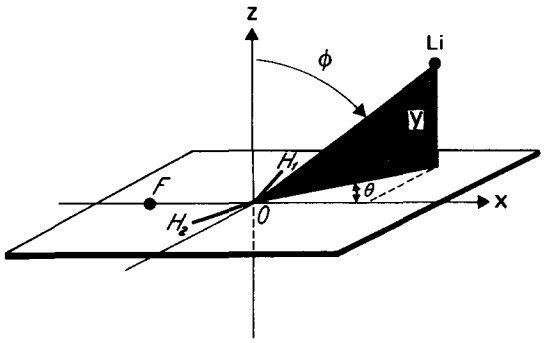

FIG. 1. Coordinate system for the H_2O–Li–F complex. The H_2O molecule and the fluorine nucleus are in the xy plane at $z=0.0$ a.u. The coordinates for the H_2O molecules are as follows: for the oxygen nucleus, $x=y=z=0.0$ a.u.; for the H(1) nucleus the coordinates are $x=-1.025738$ a.u., $y=1.4335318$ a.u., and $z=0.0$ a.u.; the coordinates of the H(2) nucleus are $x=-1.1025738$ a.u., $y=-1.4335318$ a.u., and $z=0.0$ a.u. The fluorine nucleus can assume any position in the xy plane but is constrained to $z=0.0$ a.u.; the lithum nucleus is described by the distance R(O–Li) in a.u. and by the two angles θ and φ, with the origin and rotation sense as indicated in this figure.

Both for the Li^+–H_2O complex and for the F^-–H_2O complex, a potential function has been reported previously.[8,14] Thus, within the framework of the pairwise additivity approximation, we have the potential needed to describe the H_2O–Li–F complex.

We now describe briefly the criteria used in selecting the 250 geometrical configurations of the H_2O–Li–F complex studied in this work. The main problem is that, even by constraining the molecule of water to a constant geometry (the experimental geometry at equilibrium), there still remain several degrees of freedom. These are the Cartesian coordinates of the $Li^+[X(Li), Y(Li), \text{and } Z(Li)]$ and the Cartesian coordinates of the $F^-[X(F), Y(F), \text{and } Z(F)]$. Thus, we have six-dimensional space.

In Fig. 1, we present the Cartesian axes and angles selected in our study of the complex. The water is kept at the origin of the Cartesian system (see the text in the caption to Fig. 1), the fluorine is kept in the xy plane, and the lithium is either in the xy plane or outside the plane. The lithium position is defined by the R(Li–O) distance and by the two angles θ and φ described in Fig. 1.

When the fluorine is on the x axis, then the F^-–H_2O two-body cluster has C_{2v} symmetry (the x axis is the main axis for this point group); therefore, any position chosen for the lithium nucleus with $\pm x$, $\pm y$, and $+z$ coordinates is equivalent to the lithium position with the same value for the $\pm x$ and $\pm y$ coordinates but with opposite sign for the z coordinate. Equivalently, when the lithium nucleus in on the x axis with $y=z=0.0$, any position for the fluorine nucleus (with $z=0.0$) has a symmetry-generated equivalent position. Other symmetry rules can be generated in a similar manner; in this way, the 250 points computed sample the space at about 600 different positions.

A significant simplification to the problem of a proper sampling of the many-dimensional surface of the H_2O–Li–F complex is achieved not by symmetry or other topological considerations alone, however, but by common chemical sense. Firstly, we note that the Li–F Hartree–Fock binding energy is about – 180 kcal/mole, that the Li^+–H_2O Hartree–Fock binding energy is about – 35 kcal/mole, and that the F^-–H_2O Hartree–Fock binding energy is about – 18 kcal/mole, on the average. Hence, the Li–F system has a binding energy about 5 to 6 times greater than the other systems, and hence the energetics of the Li–F system will dominate the complex. If we wish to use a very simple viewpoint, we could say that the H_2O–Li–F system is really no more than a perturbed Li–F system, the perturbation being written as Li^+–$(F–H_2O)^-$ or $(Li–H_2O)^+$–F^-, rather than Li^+–F^-. The water acts as a perturbation, though, of course, a nonnegligible one.

III. THE PAIRWISE ADDITIVITY APPROXIMATION

We can use the pairwise additivity approximation to obtain a good first estimate of the energy of the complex; in particular, we can use the energies $E(s, 2)$ and plot the energy contour diagrams for a number of planes intersecting the many-dimensional surface.

To illustrate the way in which two-body stabilization energies can be used to estimate the stabilization energy of the complex, consider the following examples. From earlier work,[3,14] it is known that when the F^-–H_2O complex is in a configuration characterized by C_{2v} symmetry, it is nearly in a minimum-energy geometry; suppose, now, that the Li^+ ion is on the C_{2v} axis (that is, the Li^+ ion is situated on the positive x axis in Fig. 1); then the Hartree–Fock energy of stabilization will be about – 35 kcal/mole for the H_2O–Li^+ complex, plus about – 16 kcal/mole for the F^-–H_2O complex, plus a stabilization energy for the Li–F complex amounting to about – 75 or – 80 kcal/mole (due to the Li–F interaction at a distance of about 8 a.u.); hence, we expect a total stabilization energy of about – 128 kcal/mole. On the other hand, for the same position of the F^-–H_2O complex as described above, the minimum energy of stabilization will be obtained when the Li^+ is near the F^-–H_2O complex, but on the negative side of the x axis at about 3.0 a.u. from the fluorine. In this case, the energy for the Li–F–H_2O complex will be about – 181 kcal/mole from the Li–F fragment, plus – 16 kcal/mole from the F^-–H_2O fragment, and essentially 0 kcal/mole for the Li^+–H_2O fragment (since the Li^+ ion is too far from the H_2O molecule to give a contribution). Consequently, for the Li–F–H_2O complex, one might expect a Hartree–Fock stabilization energy of about – 197 kcal/mole.

Let us consider now the case of the H_2O–F^- complex with the fluorine near to the oxygen (positive value of x in Fig. 1), but sufficiently far removed from it to allow the Li^+ ion to insert itself in between the oxygen and the fluorine (note that the C_{2v} symmetry of the complex is preserved). The stabilization energy for the H_2O–Li^+ complex is then about – 35 kcal/mole, about – 181 kcal/mole for the Li^+–F^- complex, and essentially 0 kcal/mole for the H_2O–F^- complex. The total stabilization energy for the H_2O–Li–F complex in this

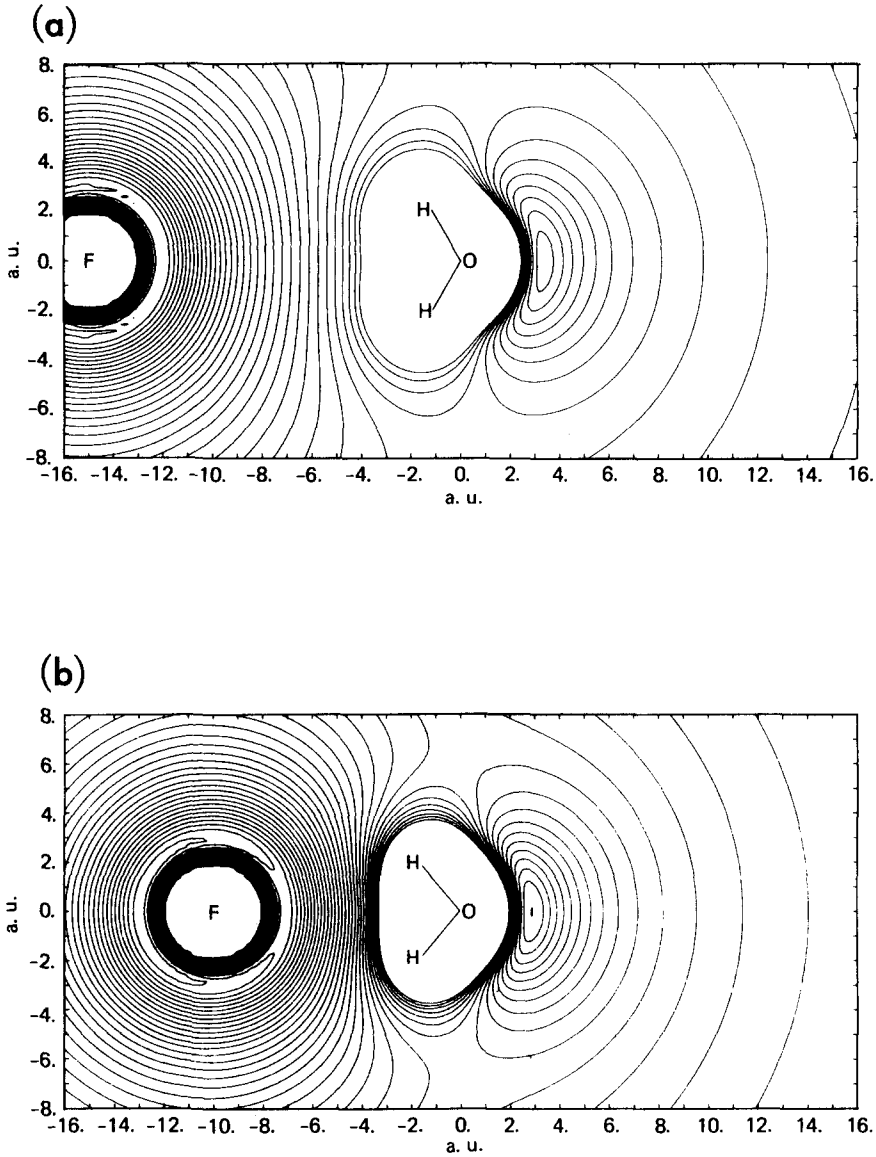

FIG. 2. Contour energy maps (at intervals of 5 kcal/mole) in the pairwise additivity approximation. The lithum nucleus is constrained to the xy plane with $z = 0.0$ a.u. The two positions of the fluorine nucleus are at $x = -15.0$ a.u. and at $x = -10.0$ a.u. (top and bottom map). The water molecule is fixed, as indicated in Fig. 1. The energy difference between contours is 5.0 kcal/mole. There are two minima in each plot: the deepest to the left of the fluorine, the second to the right of the water molecule. The dark ring surrounding the F ion results from the near superposition of many contour lines, representing the repulsive core of the ion. Such contours have not been given for the entire core, for graphic reasons. The repulsive region around H_2O is less marked, but visible to the right of the H_2O in insert (a) and both to the right and to the left of H_2O in insert (b).

geometry is -215 kcal/mole.

A third possible geometry for the H_2O-F^- complex occurs when the fluorine is hydrogen bonded to the H_2O molecule. Although the stabilization energy of the H_2O-F^- complex is a bit larger[14] (from -16 to -22 kcal/mole), the Li^+ ion in this geometry will be in an unfavorable position to interact with the water molecule. Hence, we still lose 35 kcal/mole of stabilization energy, and obtain, once again, essentially -203 kcal/mole for the Hartree–Fock stabilization energy for the $Li-F-H_2O$ complex.

In Figs. 2–6, we present a number of isoenergy maps obtained using the pairwise additivity assumption. In these figures, for a fixed position of the fluorine ion and the water molecule in the xy plane at $z = 0.0$ a.u., the lithium can assume any position in the xy plane at $z = 0.0$ a.u. In addition, in Figs. 4–6 contour diagrams are included in which the Li^+ ion can assume any position in the xy plane at $z = 2.0$ a.u., or in the xy plane at $z = 4.0$ a.u., the fluorine ion and the water molecule being fixed in the same configuration as above. The contour diagrams are obtained from the analytical potentials (see Refs. 14 and 9, and the second section of this paper).

In Fig. 2 the water molecule is centered at the origin of the Cartesian system, and the fluorine ion is placed, respectively, at -15.00 a.u. and -10.00 a.u. on the x axis. The two-body stabiliziation energies $E(s, 2)$ for the best lithium position are -181.31 kcal/mole and -182.57 kcal/mole, respectively. The interval between each contour plotted in the maps is 5 kcal/mole; successive contours are so close that purely repulsive contours were not plotted, since they would not be resolved in the maps. The stabilization energies obtained for these two cases are quite reasonable if we keep in mind that the stabilization energy of Li–F (relative to F^- and Li^+) is -181 kcal/mole.

In Fig. 3 the water molecule is kept at the origin of the coordinate system, but the fluorine ion is positioned on the positive x axis at 10.00 a.u. and at 15.00 a.u. The lithium nucleus can assume any position in the xy plane at $z = 0.0$ a.u. Again, the interval between successive contours is 5.0 kcal/mole. For the best lithium

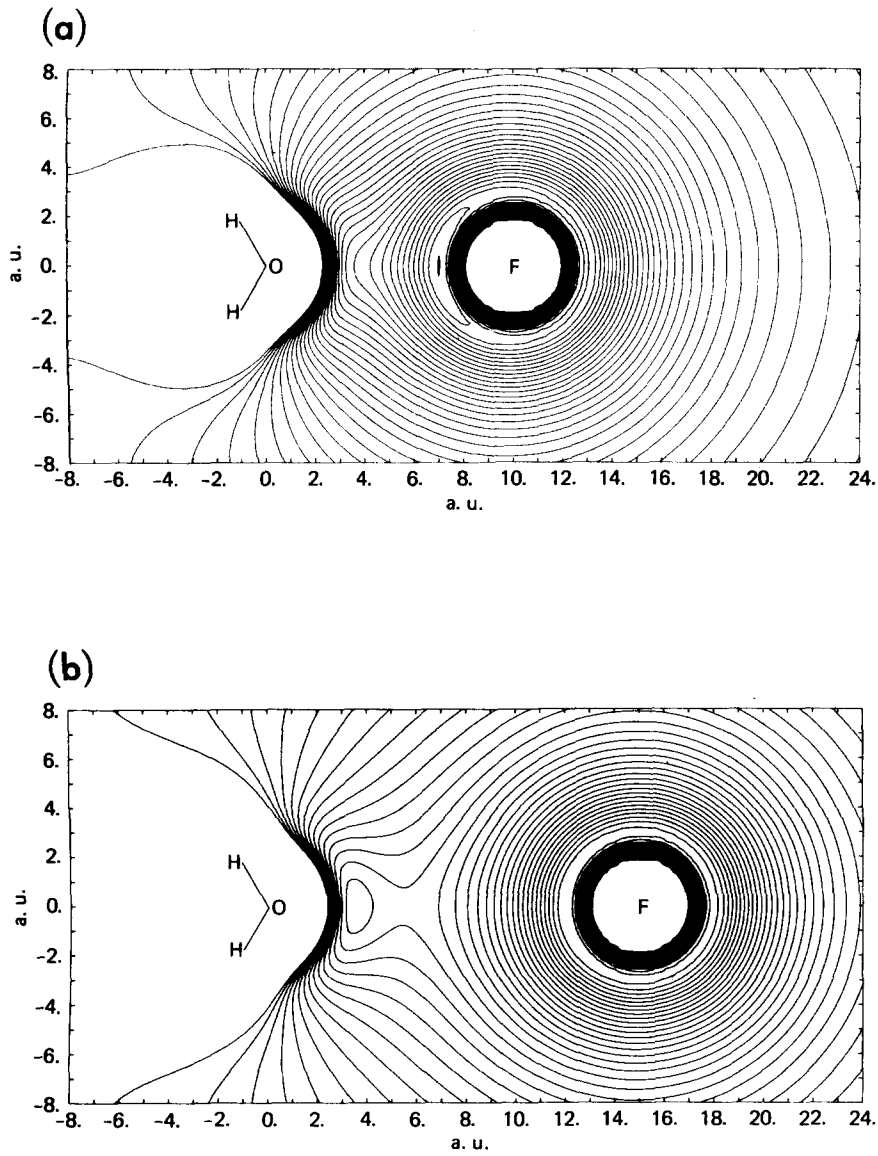

FIG. 3. Contour energy maps in the pairwise-addivity approximation. The lithium nucleus is constrained in the xy plane at $z = 0.0$ a.u. The contour interval is 5 kcal/mole. The two positions of the fluorine nucleus are at $x = +10.0$ a.u. and $x = +15.0$ a.u.; the water molecule is fixed as indicated in Fig. 1. There is only one energy minimum (in the region analyzed) located on the O–F axis, at the minimum position, the Li ion makes the most stable structure, among those considered for the complex in insert (a) and (b) of the figure.

position, the $E(s, 2)$ corresponding to these two cases is -190.20 kcal/mole and -183.34 kcal/mole, respectively. The value of $E(s, 2)$ is again very near to what we expect for the total system.

In Fig. 4 we present contour maps for the H_2O–Li–F complex when the fluorine nucleus is positioned on the negative x axis at -5.15 a.u. (note that in this geometry the fluorine is in the proper position for the H_2O–F^- complex). The three maps presented are for the lithium ion in the xy plane at $z = 0.0$ a.u., in the xy plane at $z = 2.0$ a.u., and in the xy plane at $z = 4.0$ a.u. The corresponding stabilization energies are -185.58 kcal/mole, -184.89 kcal/mole, and -161.14 kcal/mole, respectively. This set of data is of particular interest. Consider the geometries corresponding to the stabilization energies -185.58 kcal/mole and -184.89 kcal/mole; in the first geometry the Li^+ ion is on the negative x axis at the proper Li–F distance (see Fig. 4), whereas in the second geometry the Li^+ ion is (nearly) above the fluorine nucleus. Apparently, the relative position between the Li^+ ion and the water molecule is not as favorable in the second case as in the first. For the case when the lithium is in the xy plane at $z = 4.0$ a.u., the main interaction is between the Li^+ ion and the F^- ion. From Table I we see that at $R(\text{Li–F}) = 4.0$ a.u., the stabilization energy for Li–F is about -150 kcal/mole; hence, at $R(\text{Li–F}) = 4.0$ a.u., the water molecule is only a small perturbation on the Li–F molecule, of the order of about 11 kcal/mole. [In the contour map (at the bottom of the figure) the lithium nucleus is directly above the fluorine nucleus.]

In Fig. 5 we consider the case of the fluorine ion placed not in a configuration having C_{2v} symmetry relative to the water molecule, but rather in a configuration in which a hydrogen bond can form between the F^- ion and the water molecule. The coordinates of the fluorine ion in this case are $x = -3.66$ a.u., $y = 4.76$ a.u., and $z = 0.0$ a.u.[3,14] Notice that we have not displaced the fluorine ion about 4° from a linear-hydrogen-bond configuration, the geometry found to be optimal for the H_2O–F^- complex[3]; such a small deviation from a straight bond will not change our contour maps. Once

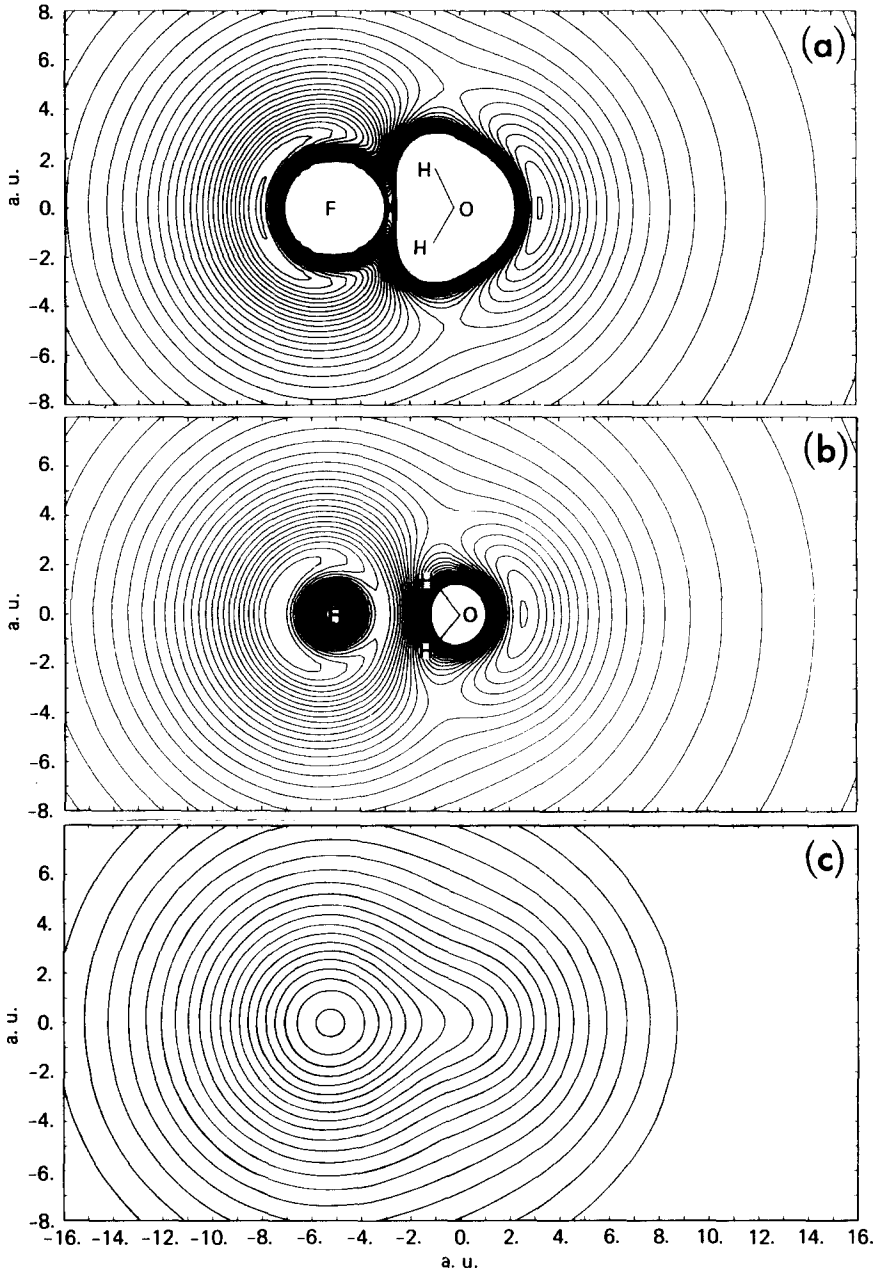

FIG. 4. Contour energy maps in the pairwise-additivity approximation. The fluorine nucleus is at $x = -5.15$ a.u., and the water molecule is fixed as indicated in Fig. 1. The three maps correspond to the lithium nucleus in the xy plane with $z = 0.0$ a.u. (top map), in the xy plane with $z = 2.0$ a.u. (middle map), and in the xy plane with $z = 4.0$ a.u. (bottom map). The interval between contours is 5.0 kcal/mole. For the (a) and (b) maps, there are two minima (as for the case of Fig. 2); one to the left of the fluorine ion, the second to the right of the water molecule. There is only one minimum in the bottom map.

again, the lithium can be positioned in the xy plane at $z = 0.0$ a.u., or in the xy plane at $z = 2.0$ a.u., or in the xy plane at $z = 4.0$ a.u. The stabilization energies $E(s, 2)$ are, respectively, -190.74 kcal/mole, -189.90 kcal/mole, and -165.00 kcal/mole. The gain of about 5 kcal/mole for these three cases relative to the three cases plotted in Fig. 4 is due to the decrease in the Li–O distance, to the increase in one of the Li–H distances, and to the hydrogen bonded position of the fluorine ion (the latter factor is of dominant importance). One of the more interesting features of the contour map at $z = 2.0$ a.u. is that the hydrogen atom of the water molecule (the one which is hydrogen bonded to the fluorine ion) has its interaction nearly totally masked by the Li–F interaction.

Figure 6 is equivalent to Fig. 4, but here the fluorine ion is situated at $x = +5.15$ a.u.

IV. HARTREE–FOCK TOTAL ENERGIES FOR THE H_2O-Li-F COMPLEX

In Table II we report the Hartree–Fock total energy for the 250 configurations we have selected. In this table, the first column is an identification number for the geometry; this identification number is also used in Table III. Columns 2–4 report the Cartesian coordinates (in a.u.) for the Li^+ ion; the following three columns (5–7) report the Cartesian coordinates for the F^- ion. The coordinates of the water molecule are held constant; the oxygen nucleus is at the origin of the Cartesian system, the first hydrogen is situated at $x = -1.1025738$ a.u., $y = 1.4335318$ a.u., and $z = 0.0$ a.u., and the second hydrogen is situated at $x = -1.1025738$ a.u., $y = -1.4335318$ a.u., and $z = 0.0$ a.u. The eighth column of Table II gives the total Hartree–Fock energy in a.u. The ninth column gives the stabilization energy

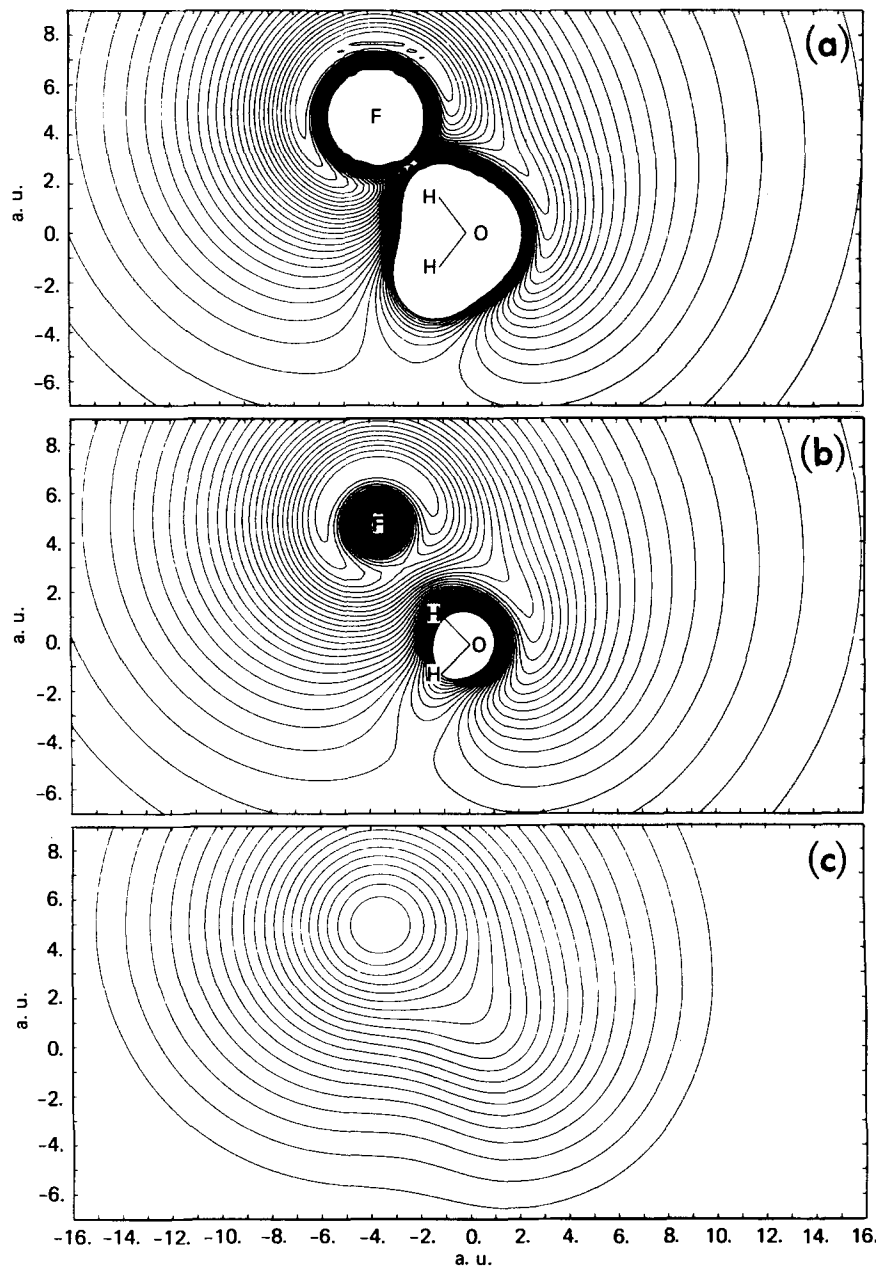

FIG. 5. Contour energy maps in the pairwise-additivity approximation. The fluorine nucleus is in the hydrogen-bonded position (see text). The water molecule is fixed as indicated in Fig. 1. The three maps correspond to the lithium nucleus in the xy plane with $z = 0.0$ a.u. (top map), with $z = 2.0$ a.u. (middle map), and with $z = 4.0$ a.u. (bottom map). The contour interval is 5.0 kcal/mole. There is only one minimum [approximately along the F–H–O bond for maps (a) and (b), and at the fluorine position for map (c)].

(in kcal/mole) of the H_2O–Li–F complex relative to the water molecule [$V(H_2O) = -76.0552619$ a.u.], the fluorine ion [$V(F^-) = -99.4582356$ a.u.], and the lithium ion [$V(Li^+) = -7.236346$ a.u.]. The last five columns report in kcal/mole the stabilization energies for the Li–F molecule, the H_2O–Li^+ complex, the H_2O–F^- complex, the sum of these quantities [i.e., $E(s, 2)$], and the difference between the total Hartree–Fock stabilization energy $E(s, \text{tot})$ and $E(s, 2)$, namely, $E(s, 3)$. The energies tabulated for the H_2O–Li^+ and H_2O–F^- complexes were obtained using the basis sets reproduced in Tables A. I, A. II, and A. III of the Appendix, and therefore represent computations independent from those reported in Refs. 1 and 3. We remark that the basis set used in this paper for the Li^+ ion is somewhat better than the one used previously.

Although, for the most part, the magnitude of the energy $E(s, 3)$ is small relative to the total stabiliziation energy, there are cases where it is comparable to the water–water stabilization energy (5 ± 1 kcal/mole). Thus, in the study of the Li^+ and F^- pair in water, the three-body correction $E(s, 3)$ might be of importance, and *cannot be neglected*, without a critical study.

In Table III we report the results of the BEA study. The number appearing in the first column of this table is an identification number for the geometry of the complex (see Table II). All energies in the table are reported in kcal/mole, except the total Hartree–Fock energy, which is given in a.u. The quantities $E(Li^+)$, $E(F^-)$, and $E(H_2O)$ are just the $P(Li^+)$, $P(F^-)$, and $P(H_2O)$ defined in Eq. (5a); these energies represent the full perturbation of the one-body energies in the complex. The quantities $E(\text{Li–F})$, $E(\text{Li–}H_2O)$, and $E(\text{F–}H_2O)$ are the $\mathcal{E}(ij)$ terms from BEA; that is, they represent the

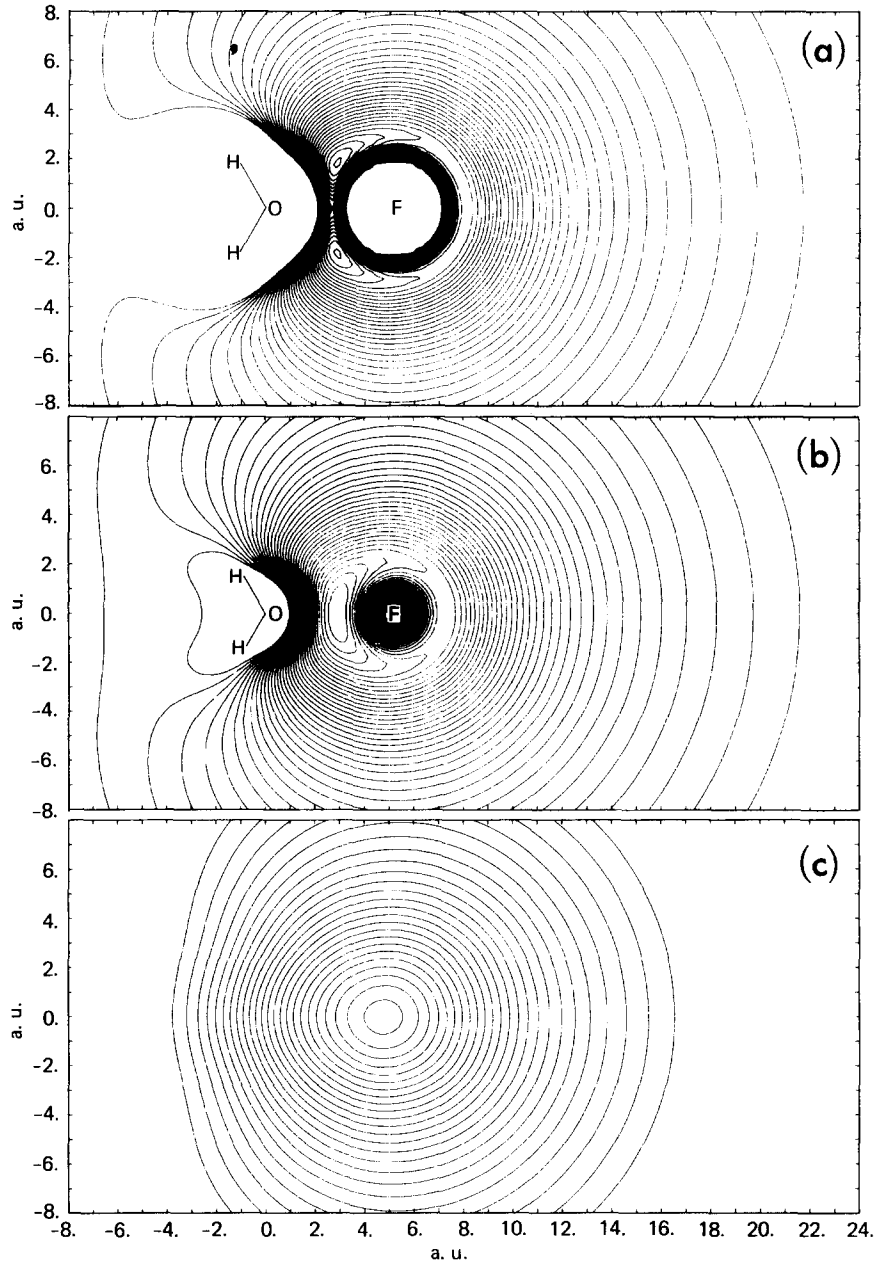

FIG. 6. Contour energy maps in the pairwise-additivity approximation. This is equivalent to Fig. 4 but the fluorine is at $x = +5.15$ a.u. There are two minima (case a) between oxygen and fluorine, one minimum (case b) on the fluorine oxygen axis, one minimum (case c) at the fluorine xy position.

two-body interactions in the complex. The term $E(\text{Li–F–H}_2\text{O})$ is the "nonclassical" BEA $\delta(ijk)$ three-body term; hence, the total stabilization energy is easily calculated from Table III as $E(s, \text{tot}) = E(\text{Li}^+) + E(\text{F}^-) + E(\text{H}_2\text{O}) + E(\text{Li–F}) + E(\text{Li–H}_2\text{O}) + E(\text{F–H}_2\text{O}) + E(\text{Li–F–H}_2\text{O})$. From Table III we have excluded those configurations where either two or all three bodies are sufficiently near one another that the basis set would introduce uncontrolled errors in the energy partitioning (the full set of data is, however, available[11b]).

Let us compare some of the quantities from Table II with corresponding quantities from Table III. We select the computations with identification numbers 5, 13, 18. Note that for all these cases, $y = z = 0.0$ a.u., both for the fluorine ion and the lithium ion. The first part of our analysis is devoted to results obtained using the classical decomposition of the total energy [see Eqs. (1)–(3)]. The second part of our analysis is devoted to results obtained using the BEA partitioning of the total energy.

It should be noted that, strictly speaking, it is quantum-mechanically incorrect to use the classical decomposition of the total energy. Indeed, the Hartree–Fock total stabilization energy is obtained from a wavefunction and a Hamiltonian that are *not* the product and the sum, respectively, of two-body wavefunctions and Hamiltonians. Only if one were to obtain an energy and a wavefunction for the $\text{H}_2\text{O–Li–F}$ complex from a *perturbation* theory based on two-body wavefunctions might the classical decomposition have an unambiguous quantum-mechanical analog. Therefore, to use Hartree–Fock results to derive an $E(s, 2)$ and an $E(s, 3)$ is somewhat unsound quantum mechanically, though most appealing physically.

TABLE II. Cartesian coordinates and Hartree–Fock energy quantities for the Li–F–H_2O complex.

Point	Cartesian coordinates (a. u.)						Total Hartree–Fock energy (a. u.)	Hartree–Fock binding energy (kcal/mole)					
	X(Li)	Y(Li)	Z(Li)	X(F)	Y(F)	Z(F)		$LiFH_2O$	LiF	LiH_2O	FH_2O	Sum of two-body	Difference
1	2.000	0.0	0.0	−3.000	0.0	0.0	−182.4584770	182.836	−128.502	173.938	150.483	195.920	−13.084
2	2.531	2.531	0.0	−3.000	0.0	0.0	−182.7502784	−0.270	−105.415	−24.402	150.483	20.666	−20.937
3	−7.500	0.0	0.0	−3.000	0.0	0.0	−182.7237963	16.347	−142.016	8.354	150.483	16.821	−0.474
4	2.000	0.0	0.0	−5.150	0.0	0.0	−182.6515541	61.679	−89.133	173.938	−16.554	68.251	−6.572
5	3.580	0.0	0.0	−5.150	0.0	0.0	−182.9632595	−133.917	−72.431	−36.302	−16.554	−125.288	−8.629
6	2.531	2.531	0.0	−5.150	0.0	0.0	−182.9505370	−125.933	−78.403	−24.402	−16.554	−119.359	−6.574
7	0.0	3.580	0.0	−5.150	0.0	0.0	−182.9055498	−97.704	−102.136	20.837	−16.554	−97.853	0.149
8	−2.531	2.531	0.0	−5.150	0.0	0.0	−182.8935571	−90.178	−168.282	89.702	−16.554	−95.135	4.957
9	7.500	0.0	0.0	−5.150	0.0	0.0	−182.8757409	−78.999	−49.585	−9.971	−16.554	−76.109	−2.889
10	5.303	5.303	0.0	−5.150	0.0	0.0	−182.8754091	−78.790	−53.557	−6.541	−16.554	−76.652	−2.138
11	0.0	7.500	0.0	−5.150	0.0	0.0	−182.9840723	−84.227	−69.406	1.736	−16.554	−84.223	−0.003
12	−5.303	5.303	0.0	−5.150	0.0	0.0	−182.9528046	−127.356	−121.174	7.844	−16.554	−129.883	2.527
13	−7.500	0.0	0.0	−5.150	0.0	0.0	−182.9875583	−149.164	−144.984	8.354	−16.554	−153.184	4.020
14	15.000	0.0	0.0	−5.150	0.0	0.0	−182.8307308	−50.755	−31.205	−2.407	−16.554	−50.166	−0.588
15	10.607	10.607	0.0	−5.150	0.0	0.0	−182.8321776	−51.662	−33.075	−1.594	−16.554	−51.223	−0.440
16	0.0	15.000	0.0	−5.150	0.0	0.0	−182.8388667	−55.860	−39.541	0.291	−16.554	−55.805	−0.055
17	−10.607	10.607	0.0	−5.150	0.0	0.0	−182.8564526	−66.895	−52.619	1.878	−16.554	−67.295	0.400
18	−15.000	0.0	0.0	−5.150	0.0	0.0	−182.8732456	−77.433	−63.957	2.365	−16.554	−78.146	0.713
19	2.000	0.0	0.0	−7.500	0.0	0.0	−182.6000211	94.016	−66.380	173.938	−9.860	97.698	−3.682
20	3.580	0.0	0.0	−7.500	0.0	0.0	−182.9203756	−107.007	−56.708	−36.302	−9.860	−102.871	−4.136
21	2.531	2.531	0.0	−7.500	0.0	0.0	−182.9065685	−98.343	−60.817	−24.402	−9.860	−95.079	−3.264
22	0.0	3.580	0.0	−7.500	0.0	0.0	−182.3541151	−65.428	−76.222	20.837	−9.860	−65.245	−0.183
23	−2.531	2.531	0.0	−7.500	0.0	0.0	−182.8020970	−32.787	−115.241	89.702	−9.860	−35.399	2.613
24	−3.580	0.0	0.0	−7.500	0.0	0.0	−182.9594291	−131.513	−159.689	33.299	−9.860	−136.249	4.736
25	7.500	0.0	0.0	−7.500	0.0	0.0	−182.8501810	−62.960	−41.797	−9.971	−9.860	−61.628	−1.332
26	5.303	5.303	0.0	−7.500	0.0	0.0	−182.8497381	−62.682	−45.241	−6.541	−9.860	−61.642	−1.040
27	0.0	7.500	0.0	−7.500	0.0	0.0	−182.8575351	−67.574	−59.290	1.736	−9.860	−67.413	−0.161
28	−5.303	5.303	0.0	−7.500	0.0	0.0	−182.9297153	−112.868	−111.888	7.844	−9.860	−113.904	1.036
29	15.000	0.0	0.0	−7.500	0.0	0.0	−182.8143403	−40.469	−28.001	−2.407	−9.860	−40.268	−0.201
30	10.607	10.607	0.0	−7.500	0.0	0.0	−182.8161288	−41.592	−29.985	−1.594	−9.860	−41.438	−0.154
31	0.0	15.000	0.0	−7.500	0.0	0.0	−182.8247770	−47.019	−37.408	0.291	−9.860	−46.977	−0.042
32	−10.607	10.607	0.0	−7.500	0.0	0.0	−182.8529128	−64.674	−56.854	1.878	−9.860	−64.836	0.162
33	−15.000	0.0	0.0	−7.500	0.0	0.0	−182.8958840	−91.638	−84.805	2.365	−9.860	−92.300	0.662
34	3.580	0.0	0.0	−15.000	0.0	0.0	−182.8669829	−73.503	−33.802	−36.302	−2.433	−72.537	−0.965
35	2.531	2.531	0.0	−15.000	0.0	0.0	−182.8503054	−63.038	−35.436	−24.402	−2.433	−62.271	−0.767
36	0.0	3.580	0.0	−15.000	0.0	0.0	−182.7854272	−22.326	−40.659	20.837	−2.433	−22.255	−0.071
37	−2.531	2.531	0.0	−15.000	0.0	0.0	−182.6983627	38.582	−49.293	89.702	−2.433	37.970	0.612
38	7.500	0.0	0.0	−15.000	0.0	0.0	−182.8145509	−40.602	−28.001	−9.971	−2.433	−40.405	−0.197
39	5.303	5.303	0.0	−15.000	0.0	0.0	−182.8121710	−39.108	−29.985	−6.541	−2.433	−38.959	−0.149
40	0.0	7.500	0.0	−15.000	0.0	0.0	−182.8106200	−38.135	−37.408	1.736	−2.433	−38.105	−0.030
41	−5.303	5.303	0.0	−15.000	0.0	0.0	−182.8315961	−51.298	−56.854	7.844	−2.433	−51.442	0.145
42	−7.500	0.0	0.0	−15.000	0.0	0.0	−182.8749383	−78.495	−84.805	8.354	−2.433	−78.885	0.390
43	15.000	0.0	0.0	−15.000	0.0	0.0	−182.7910175	−25.834	−21.143	−2.407	−2.433	−25.983	0.149
44	10.607	10.607	0.0	−15.000	0.0	0.0	−182.7924363	−26.725	−22.838	−1.594	−2.433	−26.865	0.140
45	0.0	15.000	0.0	−15.000	0.0	0.0	−182.8004186	−31.734	−29.667	0.291	−2.433	−31.809	0.076

TABLE II (*Continued*)

Point	Cartesian coordinates (a. u.) X(Li)	Y(Li)	Z(Li)	X(F)	Y(F)	Z(F)	Total Hartree-Fock energy (a. u.)	Hartree-Fock binding energy (kcal/mole) $LiFH_2O$	LiF	LiH_2O	FH_2O	Sum of two-body	Difference
46	−10.607	10.607	0.0	−15.000	0.0	0.0	−182.8379962	−55.314	−54.698	1.878	−2.433	−55.254	−0.060
47	2.531	0.0	2.531	−5.150	0.0	0.0	−182.9640117	−134.389	−78.403	−32.866	−16.554	−127.824	−6.565
48	1.790	1.790	2.531	−5.150	0.0	0.0	−182.9574441	−130.268	−83.632	−25.118	−16.554	−125.304	−4.964
49	0.0	2.531	2.531	−5.150	0.0	0.0	−182.9452855	−122.638	−102.136	−3.702	−16.554	−122.391	−0.247
50	−1.790	1.790	2.531	−5.150	0.0	0.0	−182.9672701	−136.433	−139.960	15.043	−16.554	−141.471	5.038
51	−2.531	0.0	2.531	−5.150	0.0	0.0	−183.0173939	−167.886	−168.282	10.466	−16.554	−174.370	6.484
52	5.303	0.0	5.303	−5.150	0.0	0.0	−182.8788155	−80.928	−53.557	−8.468	−16.554	−78.579	−2.349
53	3.750	3.750	5.303	−5.150	0.0	0.0	−182.8798496	−81.577	−57.033	−6.200	−16.554	−79.787	−1.790
54	0.0	5.303	5.303	−5.150	0.0	0.0	−182.8887219	−87.144	−69.406	−0.959	−16.554	−86.919	−0.225
55	−3.750	3.750	5.303	−5.150	0.0	0.0	−182.9218686	−107.944	−96.204	3.173	−16.554	−109.585	1.642
56	−5.303	0.0	5.303	−5.150	0.0	0.0	−182.9588424	−131.145	−121.174	4.176	−16.554	−133.552	2.407
57	10.607	0.0	10.607	−5.150	0.0	0.0	−182.8326401	−51.953	−33.075	−1.872	−16.554	−51.501	−0.452
58	7.500	7.500	10.607	−5.150	0.0	0.0	−182.8340608	−52.844	−34.626	−1.319	−16.554	−52.499	−0.345
59	0.0	10.607	10.607	−5.150	0.0	0.0	−182.8394259	−56.211	−39.541	−0.043	−16.554	−56.138	−0.073
60	−7.500	7.500	10.607	−5.150	0.0	0.0	−182.8498348	−62.742	−47.501	1.083	−16.554	−62.971	0.229
61	−10.607	0.0	10.607	−5.150	0.0	0.0	−182.8571161	−67.311	−52.619	1.480	−16.554	−67.693	0.382
62	2.531	0.0	2.531	−7.500	0.0	0.0	−182.9201100	−106.840	−60.817	−32.866	−9.860	−103.543	−3.297
63	1.790	1.790	2.531	−7.500	0.0	0.0	−182.9122514	−101.909	−64.334	−25.118	−9.860	−99.312	−2.597
64	0.0	2.531	2.531	−7.500	0.0	0.0	−182.8936289	−90.223	−76.222	−3.702	−9.860	−89.784	−0.440
65	−1.790	1.790	2.531	−7.500	0.0	0.0	−182.8952982	−91.271	−98.466	15.043	−9.860	−93.283	2.012
66	−2.531	0.0	2.531	−7.500	0.0	0.0	−182.9276434	−111.568	−115.241	10.466	−9.860	−114.635	3.067
67	5.303	0.0	5.303	−7.500	0.0	0.0	−182.8529561	−64.701	−45.241	−8.468	−9.860	−63.569	−1.132
68	3.750	3.750	5.303	−7.500	0.0	0.0	−182.8538312	−64.250	−48.276	−6.200	−9.860	−64.336	−0.914
69	0.0	5.303	5.303	−7.500	0.0	0.0	−182.8620107	−70.383	−59.290	−0.959	−9.860	−70.109	−0.274
70	−3.750	3.750	5.303	−7.500	0.0	0.0	−182.8946449	−90.861	−84.805	3.173	−9.860	−91.492	0.632
71	−5.303	0.0	5.303	−7.500	0.0	0.0	−182.9357134	−116.631	−111.888	4.176	−9.860	−117.572	0.941
72	10.607	0.0	10.607	−7.500	0.0	0.0	−182.8165833	−41.877	−29.985	−1.872	−9.860	−41.716	−0.161
73	7.500	7.500	10.607	−7.500	0.0	0.0	−182.8183532	−42.988	−31.680	−1.319	−9.860	−42.859	−0.129
74	0.0	10.607	10.607	−7.500	0.0	0.0	−182.8253263	−47.363	−37.408	−0.043	−9.860	−47.311	−0.053
75	−7.500	7.500	10.607	−7.500	0.0	0.0	−182.8406965	−57.008	−48.276	1.083	−9.860	−57.053	0.045
76	−10.607	0.0	10.607	−7.500	0.0	0.0	−182.8535661	−65.084	−56.854	1.480	−9.860	−65.234	0.150
77	2.531	0.0	2.531	−15.000	0.0	0.0	−182.8638097	−71.512	−35.436	−32.866	−2.433	−70.735	−0.776
78	1.790	1.790	2.531	−15.000	0.0	0.0	−182.8533056	−64.920	−36.749	−25.118	−2.433	−64.300	−0.620
79	0.0	2.531	2.531	−15.000	0.0	0.0	−182.8246436	−46.935	−40.659	−3.702	−2.433	−46.794	−0.141
80	−1.790	1.790	2.531	−15.000	0.0	0.0	−182.8027064	−33.169	−46.208	15.043	−2.433	−33.598	0.429
81	−2.531	0.0	2.531	−15.000	0.0	0.0	−182.8144629	−40.546	−49.298	10.466	−2.433	−41.265	0.719
82	5.303	0.0	5.303	−15.000	0.0	0.0	−182.8152762	−41.057	−29.985	−8.468	−2.433	−40.886	−0.171
83	3.750	3.750	5.303	−15.000	0.0	0.0	−182.8143120	−40.452	−31.680	−6.200	−2.433	−40.313	−0.138
84	0.0	5.303	5.303	−15.000	0.0	0.0	−182.8149606	−40.859	−37.408	−0.959	−2.433	−40.800	−0.058
85	−3.750	3.750	5.303	−15.000	0.0	0.0	−182.8255484	−47.503	−48.276	3.173	−2.433	−47.537	0.034
86	−5.303	0.0	5.303	−15.000	0.0	0.0	−182.8374960	−54.998	−56.854	4.176	−2.433	−55.111	0.113
87	10.607	0.0	10.607	−15.000	0.0	0.0	−182.7928826	−27.005	−22.836	−1.872	−2.433	−27.143	0.138
88	7.500	7.500	10.607	−15.000	0.0	0.0	−182.7943903	−27.951	−24.326	−1.319	−2.433	−28.078	0.127
89	0.0	10.607	10.607	−15.000	0.0	0.0	−182.8009552	−32.070	−29.667	−0.043	−2.433	−32.143	0.073
90	−7.500	7.500	10.607	−15.000	0.0	0.0	−182.8186696	−43.186	−41.797	1.083	−2.433	−43.147	−0.039

TABLE II (*Continued*)

Point	Cartesian coordinates (a. u.)						Total Hartree–Fock energy (a. u.)	Hartree–Fock binding energy (kcal/mole)					
	X(Li)	Y(Li)	Z(Li)	X(F)	Y(F)	Z(F)		$LiFH_2O$	LiF	LiH_2O	FH_2O	Sum of two-body	Difference
91	−10.607	0.0	10.607	−15.000	0.0	0.0	−182.8386369	−55.716	−54.693	1.480	−2.433	−55.652	−0.064
92	0.0	0.0	3.580	−3.000	0.0	0.0	−182.7562230	−4.001	−137.189	−18.393	150.483	−5.099	1.098
93	0.0	0.0	3.580	−5.150	0.0	0.0	−182.9689316	−137.476	−102.136	−18.393	−16.554	−137.083	−0.393
94	0.0	0.0	7.500	−5.150	0.0	0.0	−182.8929734	−89.812	−69.406	−3.430	−16.554	−89.390	−0.422
95	0.0	0.0	15.000	−5.150	0.0	0.0	−182.8399718	−56.553	−39.541	−0.369	−16.554	−56.464	−0.089
96	0.0	0.0	3.580	−7.500	0.0	0.0	−182.9173311	−105.097	−76.222	−18.393	−9.860	−104.476	−0.621
97	0.0	0.0	7.500	−7.500	0.0	0.0	−182.8661071	−72.953	−59.290	−3.430	−9.860	−72.580	−0.374
98	0.0	0.0	15.000	−7.500	0.0	0.0	−182.8258624	−47.700	−37.408	−0.369	−9.860	−47.636	−0.063
99	0.0	0.0	3.580	−15.000	0.0	0.0	−182.8481444	−61.682	−40.659	−18.393	−2.433	−61.486	−0.196
100	0.0	0.0	7.500	−15.000	0.0	0.0	−182.8189369	−43.354	−37.408	−3.430	−2.433	−43.271	−0.083
101	0.0	0.0	15.000	−15.000	0.0	0.0	−182.8014792	−32.399	−29.667	−0.369	−2.433	−32.469	0.070
102	0.0	0.0	2.000	5.150	0.0	0.0	−182.5588818	119.831	−116.332	214.900	18.095	116.663	3.169
103	0.0	0.0	7.500	5.150	0.0	0.0	−182.8366105	−54.444	−69.406	−3.430	18.095	−54.741	0.297
104	0.0	0.0	15.000	5.150	0.0	0.0	−182.7845872	−21.799	−39.541	−0.369	18.095	−21.815	0.016
105	0.0	0.0	15.000	7.500	0.0	0.0	−182.7961134	−29.032	−37.408	−0.369	8.751	−29.025	−0.007
106	0.0	0.0	2.000	7.500	0.0	0.0	−182.5224177	142.713	−81.827	214.900	8.751	141.824	0.888
107	0.0	0.0	3.580	7.500	0.0	0.0	−182.8858939	−85.370	−76.222	−18.393	8.751	−85.864	0.495
108	0.0	0.0	7.500	7.500	0.0	0.0	−182.8357971	−53.934	−59.290	−3.430	8.751	−53.968	0.035
109	1.414	0.0	1.414	5.150	0.0	0.0	−182.6637483	54.027	−157.351	186.741	18.095	47.484	6.544
110	1.000	1.000	1.414	5.150	0.0	0.0	−182.6319942	73.953	−142.105	192.122	18.095	68.112	5.842
111	0.0	1.414	1.414	5.150	0.0	0.0	−182.4810023	168.701	−116.332	264.839	18.095	166.602	2.100
112	−1.000	1.000	1.414	5.150	0.0	0.0	−182.3140066	273.491	−100.196	356.827	18.095	274.726	−1.234
113	−1.414	0.0	1.414	5.150	0.0	0.0	−182.4138397	210.846	−95.155	290.747	18.095	213.687	−2.841
114	2.531	0.0	2.531	5.150	0.0	0.0	−183.0300257	−175.813	−168.282	−32.866	18.095	−183.054	7.242
115	1.790	1.790	2.531	5.150	0.0	0.0	−182.8742154	−140.792	−139.960	−25.118	18.095	−146.983	6.191
116	0.0	2.531	2.531	5.150	0.0	0.0	−182.8874218	−86.328	−102.136	−3.702	18.095	−87.743	1.414
117	−1.790	1.790	2.531	5.150	0.0	0.0	−182.8354847	−53.738	−83.632	15.043	18.095	−50.495	−3.243
118	−2.531	0.0	2.531	5.150	0.0	0.0	−182.8374438	−54.967	−78.403	10.466	18.095	−49.843	−5.124
119	5.303	0.0	5.303	5.150	0.0	0.0	−182.9255333	−110.243	−121.174	−8.468	18.095	−111.548	1.304
120	3.750	3.750	5.303	5.150	0.0	0.0	−182.8822694	−83.095	−96.204	−6.200	18.095	−84.310	1.215
121	0.0	5.303	5.303	5.150	0.0	0.0	−182.8328682	−52.096	−69.406	−0.959	18.095	−52.270	0.175
122	−3.750	3.750	5.303	5.150	0.0	0.0	−182.8087886	−36.986	−57.033	3.173	18.095	−35.765	−1.220
123	−5.303	0.0	5.303	5.150	0.0	0.0	−182.8025037	−33.042	−53.557	4.176	18.095	−31.286	−1.756
124	10.607	0.0	10.607	5.150	0.0	0.0	−182.8076831	−36.292	−52.619	−1.872	18.095	−36.396	0.104
125	7.500	7.500	10.607	5.150	0.0	0.0	−182.7986422	−30.619	−47.501	−1.319	18.095	−30.725	0.106
126	0.0	10.607	10.607	5.150	0.0	0.0	−182.7841013	−21.494	−39.541	−0.043	18.095	−21.490	−0.005
127	−7.500	7.500	10.607	5.150	0.0	0.0	−182.7747600	−15.633	−34.626	1.083	18.095	−15.448	−0.184
128	−10.607	0.0	10.607	5.150	0.0	0.0	−182.7717824	−13.764	−33.075	1.480	18.095	−13.501	−0.263
129	1.000	1.000	1.414	7.500	0.0	0.0	−182.5768035	108.586	−94.978	192.122	8.751	105.895	2.691
130	0.0	1.414	1.414	7.500	0.0	0.0	−182.4436225	192.157	−81.827	264.839	8.751	191.763	0.394
131	−1.000	1.000	1.414	7.500	0.0	0.0	−182.2855425	291.353	−72.909	356.827	8.751	292.669	−1.316
132	−1.414	0.0	1.414	7.500	0.0	0.0	−182.3875530	227.341	−69.979	290.747	8.751	229.520	−2.179
133	2.531	0.0	2.531	7.500	0.0	0.0	−182.9660550	−135.671	−115.241	−32.866	8.751	−139.356	3.685
134	1.790	1.790	2.531	7.500	0.0	0.0	−182.9285170	−112.116	−98.466	−25.118	8.751	−114.832	2.717
135	0.0	2.531	2.531	7.500	0.0	0.0	−182.8628896	−70.934	−76.222	−3.702	8.751	−71.172	0.238

TABLE II (*Continued*)

Point	Cartesian coordinates (a. u.) X(Li)	Y(Li)	Z(Li)	X(F)	Y(F)	Z(F)	Total Hartree–Fock energy (a. u.)	Hartree–Fock binding energy (kcal/mole) $LiFH_2O$	LiF	LiH_2O	FH_2O	Sum of two-body	Difference
136	−1.790	1.790	2.531	7.500	0.0	0.0	−182.8176663	−42.557	−64.334	15.043	8.751	−40.540	−2.016
137	−2.531	0.0	2.531	7.500	0.0	0.0	−182.8208518	−44.555	−60.817	10.466	8.751	−41.599	−2.956
138	5.303	0.0	5.303	7.500	0.0	0.0	−182.9260137	−110.545	−111.888	−8.468	8.751	−111.605	1.060
139	3.750	3.750	5.303	7.500	0.0	0.0	−182.8796575	−81.456	−84.805	−6.200	8.751	−82.254	0.798
140	0.0	5.303	5.303	7.500	0.0	0.0	−182.8319673	−51.530	−59.290	−0.959	8.751	−51.497	−0.033
141	−5.303	0.0	5.303	7.500	0.0	0.0	−182.8027833	−33.217	−45.241	4.176	8.751	−32.313	−0.904
142	10.607	0.0	10.607	7.500	0.0	0.0	−182.8294112	−49.927	−56.854	−1.872	8.751	−49.974	0.047
143	7.500	7.500	10.607	7.500	0.0	0.0	−182.8149063	−40.825	−48.276	−1.319	8.751	−40.844	0.019
144	0.0	10.607	10.607	7.500	0.0	0.0	−182.7956119	−28.717	−37.406	−0.043	9.751	−28.699	−0.018
145	−7.500	7.500	10.607	7.500	0.0	0.0	−182.7847736	−21.916	−31.680	1.083	8.751	−21.845	−0.071
146	−10.607	0.0	10.607	7.500	0.0	0.0	−182.7814796	−19.849	−29.985	1.480	8.751	−19.754	−0.096
147	3.580	0.0	0.0	5.150	0.0	0.0	−182.2217849	331.361	329.892	−36.302	18.095	311.684	19.676
148	2.531	2.531	0.0	5.150	0.0	0.0	−183.0163431	−167.227	−168.282	−24.402	18.095	−174.590	7.363
149	0.0	3.580	0.0	5.150	0.0	0.0	−182.8490659	−62.260	−102.136	20.837	18.095	−63.204	0.944
150	−2.531	2.531	0.0	5.150	0.0	0.0	−182.7103643	24.776	−78.403	89.702	18.095	29.393	−4.617
151	−3.580	0.0	0.0	5.150	0.0	0.0	−182.7962486	−29.117	−72.431	33.299	18.095	−21.037	−8.080
152	7.500	0.0	0.0	5.150	0.0	0.0	−182.9656062	−135.389	−144.984	−9.971	18.095	−136.860	1.470
153	5.303	5.303	0.0	5.150	0.0	0.0	−182.9227519	−108.498	−121.174	−6.541	18.095	−109.620	1.122
154	0.0	7.500	0.0	5.150	0.0	0.0	−182.8288080	−49.548	−69.406	1.736	18.095	−49.575	0.027
155	−5.303	5.303	0.0	5.150	0.0	0.0	−182.7971404	−29.676	−53.557	7.844	18.095	−27.618	−2.059
156	−7.500	0.0	0.0	5.150	0.0	0.0	−182.7911683	−25.929	−49.585	8.354	18.095	−23.137	−2.792
157	15.000	0.0	0.0	5.150	0.0	0.0	−182.8268249	−48.304	−63.957	−2.407	18.095	−48.269	−0.034
158	10.607	10.607	0.0	5.150	0.0	0.0	−182.8072679	−36.032	−52.619	−1.594	18.095	−36.118	0.086
159	0.0	15.000	0.0	5.150	0.0	0.0	−182.7836039	−21.182	−39.541	0.291	18.095	−21.156	−0.026
160	−10.607	10.607	0.0	5.150	0.0	0.0	−182.7711955	−13.396	−33.075	1.878	18.095	−13.103	−0.293
161	−15.000	0.0	0.0	5.150	0.0	0.0	−182.7676187	−11.152	−31.205	2.365	18.095	−10.745	−0.406
162	−1.414	1.414	0.0	7.500	0.0	0.0	−177.7520681	3136.121	−69.979	3195.813	8.751	3134.585	1.536
163	−2.000	0.0	0.0	7.500	0.0	0.0	−182.2107831	338.264	−66.380	398.670	8.751	341.042	−2.777
164	3.580	0.0	0.0	7.500	0.0	0.0	−183.0402980	−182.259	−159.689	−36.302	8.751	−187.239	4.981
165	2.531	2.531	0.0	7.500	0.0	0.0	−182.9526030	−127.230	−115.241	−24.402	8.751	−130.892	3.662
166	0.0	3.580	0.0	7.500	0.0	0.0	−182.8242105	−46.663	−76.222	20.837	8.751	−46.633	−0.030
167	−2.531	2.531	0.0	7.500	0.0	0.0	−182.6941482	34.951	−60.817	89.702	8.751	37.636	−2.685
168	−3.580	0.0	0.0	7.500	0.0	0.0	−182.7802677	−19.089	−56.708	33.299	8.751	−14.657	−4.431
169	5.303	5.303	0.0	7.500	0.0	0.0	−182.9230649	−108.694	−111.888	−6.541	8.751	−109.678	0.984
170	0.0	7.500	0.0	7.500	0.0	0.0	−182.8277906	−48.910	−59.290	1.736	8.751	−48.802	−0.108
171	−5.303	5.303	0.0	7.500	0.0	0.0	−182.7971567	−29.687	−45.241	7.844	8.751	−28.645	−1.042
172	−7.500	0.0	0.0	7.500	0.0	0.0	−182.7912930	−26.007	−41.797	8.354	8.751	−24.692	−1.315
173	15.000	0.0	0.0	7.500	0.0	0.0	−182.8747638	−78.385	−84.805	−2.407	8.751	−78.461	0.076
174	10.607	10.607	0.0	7.500	0.0	0.0	−182.8289832	−49.658	−56.854	−1.594	8.751	−49.696	0.038
175	0.0	15.000	0.0	7.500	0.0	0.0	−182.7950986	−28.395	−37.408	0.291	8.751	−28.366	−0.030
176	−10.607	10.607	0.0	7.500	0.0	0.0	−182.7808715	−19.468	−29.985	1.878	8.751	−19.355	−0.112
177	−15.000	0.0	0.0	7.500	0.0	0.0	−182.7769918	−17.033	−28.001	2.365	8.751	−16.885	−0.149
178	2.000	0.0	0.0	5.303	5.303	0.0	−182.6225132	79.903	−102.544	173.938	5.314	76.709	3.194
179	3.580	0.0	0.0	5.303	5.303	0.0	−182.9771190	−142.614	−115.241	−36.302	5.314	−146.229	3.616
180	2.531	2.531	0.0	5.303	5.303	0.0	−183.0269410	−173.877	−159.689	−24.402	5.314	−178.776	4.899

TABLE II (*Continued*)

Point	Cartesian coordinates (a. u.) X(Li)	Y(Li)	Z(Li)	X(F)	Y(F)	Z(F)	Total Hartree–Fock energy (a. u.)	Hartree–Fock binding energy (kcal/mole) $LiFH_2O$	LiF	LiH_2O	FH_2O	Sum of two-body	Difference
181	0.0	3.580	0.0	5.303	5.303	0.0	−182.8859296	−85.392	−115.241	20.837	5.314	−89.090	3.698
182	7.500	0.0	0.0	5.303	5.303	0.0	−182.9335512	−115.275	−111.888	−9.971	5.314	−116.545	1.270
183	0.0	7.500	0.0	5.303	5.303	0.0	−182.9158145	−104.145	−111.888	1.736	5.314	−104.838	0.693
184	15.000	0.0	0.0	5.303	5.303	0.0	−182.8356617	−53.849	−56.854	−2.407	5.314	−53.947	0.098
185	10.607	10.607	0.0	5.303	5.303	0.0	−182.8787517	−80.888	−84.805	−1.594	5.314	−81.085	0.197
186	0.0	15.000	0.0	5.303	5.303	0.0	−182.8314496	−51.206	−56.854	0.291	5.314	−51.249	0.043
187	2.000	0.0	0.0	0.0	7.500	0.0	−182.6082317	88.864	−81.827	173.938	−3.386	88.725	0.139
188	3.580	0.0	0.0	0.0	7.500	0.0	−182.9346057	−115.936	−76.222	−36.302	−3.386	−115.911	−0.026
189	2.531	2.531	0.0	0.0	7.500	0.0	−182.9722737	−139.573	−115.241	−24.402	−3.386	−143.029	3.456
190	0.0	3.580	0.0	0.0	7.500	0.0	−182.9676342	−136.662	−159.689	20.837	−3.386	−142.238	5.576
191	7.500	0.0	0.0	0.0	7.500	0.0	−182.8657873	−72.753	−59.290	−9.971	−3.386	−72.647	−0.106
192	5.303	5.303	0.0	0.0	7.500	0.0	−182.9417441	−120.416	−111.888	−6.541	−3.386	−121.816	1.400
193	15.000	0.0	0.0	0.0	7.500	0.0	−182.8187416	−43.231	−37.408	−2.407	−3.386	−43.201	−0.030
194	10.607	10.607	0.0	0.0	7.500	0.0	−182.8480555	−61.626	−56.854	−1.594	−3.386	−61.833	0.208
195	0.0	15.000	0.0	0.0	7.500	0.0	−182.8889914	−87.313	−84.805	0.291	−3.386	−87.901	0.588
196	2.000	0.0	0.0	−3.140	4.082	0.0	−182.6734500	47.940	−97.434	173.938	−21.554	54.951	−7.011
197	3.580	0.0	0.0	−3.140	4.082	0.0	−182.9822585	−145.839	−80.740	−36.302	−21.554	−138.596	−7.243
198	2.531	2.531	0.0	−3.140	4.082	0.0	−182.9958879	−154.391	−109.177	−24.402	−21.554	−155.133	0.742
199	0.0	3.580	0.0	−3.140	4.082	0.0	−183.0231878	−171.522	−179.812	20.837	−21.554	−180.528	9.007
200	7.500	0.0	0.0	−3.140	4.082	0.0	−182.8919270	−89.155	−55.110	−9.971	−21.554	−86.634	−2.521
201	5.303	5.303	0.0	−3.140	4.082	0.0	−182.9120130	−101.759	−74.182	−6.541	−21.554	−102.277	0.518
202	0.0	7.500	0.0	−3.140	4.082	0.0	−182.9935466	−152.922	−138.014	1.736	−21.554	−157.832	4.910
203	15.000	0.0	0.0	−3.140	4.082	0.0	−182.9427661	−58.307	−33.778	−2.407	−21.554	−57.739	−0.568
204	10.607	10.607	0.0	−3.140	4.082	0.0	−182.8522034	−64.229	−41.205	−1.594	−21.554	−64.353	0.124
205	0.0	15.000	0.0	−3.140	4.082	0.0	−182.8701770	−75.507	−55.286	0.291	−21.554	−76.549	1.042
206	2.000	0.0	0.0	−4.572	5.945	0.0	−182.6056541	90.482	−71.313	173.938	−9.506	93.120	−2.638
207	3.580	0.0	0.0	−4.572	5.945	0.0	−182.9269126	−111.109	−62.398	−36.302	−9.506	−108.206	−2.903
208	2.531	2.531	0.0	−4.572	5.945	0.0	−182.9315417	−114.014	−80.538	−24.402	−9.506	−114.446	0.432
209	0.0	3.580	0.0	−4.572	5.945	0.0	−182.9227594	−108.503	−124.869	20.837	−9.506	−113.537	5.034
210	7.500	0.0	0.0	−4.572	5.945	0.0	−182.8567544	−67.084	−46.594	−9.971	−9.506	−66.070	−1.014
211	5.303	5.303	0.0	−4.572	5.945	0.0	−182.8766779	−79.587	−63.648	−6.541	−9.506	−79.695	0.108
212	0.0	7.500	0.0	−4.572	5.945	0.0	−182.9711405	−138.862	−132.894	1.736	−9.506	−140.663	1.801
213	15.000	0.0	0.0	−4.572	5.945	0.0	−182.8180906	−42.823	−30.747	−2.407	−9.506	−42.660	−0.163
214	10.607	10.607	0.0	−4.572	5.945	0.0	−182.8304372	−50.570	−39.493	−1.594	−9.506	−50.593	0.022
215	0.0	15.000	0.0	−4.572	5.945	0.0	−182.8627774	−70.864	−62.056	0.291	−9.506	−71.271	0.407
216	2.000	0.0	0.0	−4.620	2.275	0.0	−182.6611734	55.643	−91.120	173.938	−19.551	63.267	−7.624
217	3.580	0.0	0.0	−4.620	2.275	0.0	−182.9715076	−139.092	−74.372	−36.302	−19.551	−130.225	−8.868
218	2.531	2.531	0.0	−4.620	2.275	0.0	−182.9675147	−136.587	−89.053	−24.402	−19.551	−133.005	−3.582
219	0.0	3.580	0.0	−4.620	2.275	0.0	−182.9513267	−126.429	−133.657	20.837	−19.551	−132.370	5.942
220	7.500	0.0	0.0	−4.620	2.275	0.0	−182.8827833	−83.418	−50.876	−9.971	−19.551	−80.397	−3.021
221	5.303	5.303	0.0	−4.620	2.275	0.0	−182.8899024	−87.885	−60.641	−6.541	−19.551	−86.733	−1.152
222	0.0	7.500	0.0	−4.620	2.275	0.0	−182.9206843	−107.201	−91.469	1.736	−19.551	−109.283	2.083
223	15.000	0.0	0.0	−4.620	2.275	0.0	−182.8365976	−54.436	−31.824	−2.407	−19.551	−53.782	−0.654
224	10.607	10.607	0.0	−4.620	2.275	0.0	−182.8415334	−57.533	−36.155	−1.594	−19.551	−57.299	−0.234
225	0.0	15.000	0.0	−4.620	2.275	0.0	−182.8537461	−65.197	−46.315	0.291	−19.551	−65.575	0.378

TABLE II (*Continued*)

Point	Cartesian coordinates (a. u.)						Total Hartree–Fock energy (a. u.)	Hartree–Fock binding energy (kcal/mole)					
	X(Li)	Y(Li)	Z(Li)	X(F)	Y(F)	Z(F)		$LiFH_2O$	LiF	LiH_2O	FH_2O	Sum of two-body	Difference
226	−2.531	2.531	0.0	−3.000	0.0	0.0	−182.6199904	81.486	−170.087	89.702	150.483	70.098	11.388
227	−7.500	0.0	0.0	−3.000	0.0	0.0	−182.7237963	16.347	−142.016	8.354	150.483	16.821	−0.474
228	25.000	0.0	0.0	−5.150	0.0	0.0	−182.8111525	−38.469	−21.040	−0.863	−16.554	−38.457	−0.012
229	17.678	17.678	0.0	−5.150	0.0	0.0	−182.8120677	−39.043	−21.947	−0.581	−16.554	−39.082	0.039
230	0.0	25.000	0.0	−5.150	0.0	0.0	−182.8153086	−41.077	−24.750	0.070	−16.554	−41.234	0.157
231	−17.678	17.678	0.0	−5.150	0.0	0.0	−182.8210780	−44.697	−29.057	0.655	−16.554	−44.957	0.259
232	−25.000	0.0	0.0	−5.150	0.0	0.0	−182.8248476	−47.063	−31.669	0.867	−16.554	−47.356	0.294
233	0.0	2.000	0.0	5.150	0.0	0.0	−182.2351268	322.989	−116.332	420.263	18.095	322.025	0.963
234	2.000	0.0	0.0	5.150	0.0	0.0	−182.7186911	19.551	−180.274	173.938	18.095	11.759	7.792
235	1.414	1.414	0.0	5.150	0.0	0.0	−182.6808001	43.327	−157.351	176.777	18.095	37.520	5.807
236	−1.414	1.414	0.0	5.150	0.0	0.0	−177.7733476	3122.768	−95.155	3195.813	18.095	3118.753	4.016
237	−2.000	0.0	0.0	5.150	0.0	0.0	−182.2328557	324.414	−89.133	398.670	18.095	327.632	−3.218
238	2.000	0.0	0.0	7.500	0.0	0.0	−182.6375185	70.487	−116.861	173.938	8.751	65.829	4.658
239	1.414	1.414	0.0	7.500	0.0	0.0	−182.6122524	86.341	−102.544	176.777	8.751	82.984	3.357
240	0.0	2.000	0.0	7.500	0.0	0.0	−182.1967857	347.048	−81.827	420.263	8.751	347.187	−0.139
241	1.414	0.0	1.414	7.500	0.0	0.0	−182.5962036	96.412	−102.544	186.741	8.751	92.948	3.464
242	3.580	0.0	0.0	−3.000	0.0	0.0	−182.7666050	−10.515	−97.182	−36.302	150.483	16.999	−27.514
243	−5.303	5.303	0.0	−3.000	0.0	0.0	−182.6709684	49.497	−111.064	7.844	150.483	47.263	2.234
244	−3.580	0.0	0.0	−15.000	0.0	0.0	−182.7863327	−22.895	−54.992	33.299	−2.433	−24.126	1.231
245	0.0	7.500	0.0	−3.000	0.0	0.0	−182.6332706	73.152	−78.505	1.736	150.483	73.715	−0.563
246	2.531	0.0	2.531	−3.000	0.0	0.0	−182.7623666	−7.856	−105.415	−32.866	150.483	12.202	−20.058
247	1.790	1.790	2.531	−3.000	0.0	0.0	−182.7530647	−2.019	−112.578	−25.118	150.483	12.788	−14.806
248	0.0	2.531	2.531	−3.000	0.0	0.0	−182.7334765	10.273	−137.189	−3.702	150.483	9.593	0.680
249	−1.790	1.790	2.531	−3.000	0.0	0.0	−182.7467951	1.915	−176.834	15.043	150.483	−11.308	13.223
250	−2.531	0.0	2.531	−3.000	0.0	0.0	−182.7396042	6.428	−170.087	10.466	150.483	−9.138	15.565

TABLE III. Selected geometries for the bond energy analyses (all data in kcal/mole).

Point	E(Li)	E(F)	$E(H_2O)$	E(LiF)	$E(LiH_2O)$	$E(FH_2O)$	$E(LiFH_2O)$	Total Hartree–Fock energy (a.u.)
5	−17.863	0.802	15.824	−70.180	−60.842	−10.758	9.102	−182.9632595
6	−15.339	0.077	5.528	−76.410	−43.447	−4.646	8.307	−182.9505370
12	−2.227	4.023	−18.734	−130.873	5.171	10.329	4.957	−182.9528046
13	−171.416	60.872	−8.103	−43.224	3.636	6.152	2.920	−182.9875583
18	−0.098	−4.814	−21.081	−66.271	0.771	10.176	3.886	−182.8732456
20	−17.373	0.948	31.375	−56.000	−51.170	−18.673	3.888	−182.9203756
21	−14.997	1.146	19.372	−60.337	−29.601	−15.731	1.807	−182.9065685
33	−0.549	2.206	−0.550	−86.518	2.521	−8.788	0.041	−182.8958840
34	−18.144	0.016	22.173	−33.191	−40.289	−5.534	1.467	−182.8669829
54	−0.364	−2.848	−16.253	−70.976	−8.729	6.558	5.470	−182.8887219
55	−0.857	−1.015	−17.269	−100.797	−1.932	7.912	6.017	−182.9218686
56	−2.251	3.093	−16.912	−130.459	0.984	8.750	5.651	−182.9588424
71	−1.849	8.458	0.261	−118.371	3.906	−8.605	−0.430	−182.9357134
96	−20.098	1.821	41.655	−75.266	−40.634	−18.999	6.427	−182.9173311
97	−0.358	0.903	4.544	−59.821	−8.145	−10.893	0.818	−182.8661071
119	−2.970	5.480	−12.337	−133.458	−15.681	38.211	10.511	−182.9255333
120	−1.481	−0.073	−12.540	−102.944	−12.809	37.767	8.987	−182.8822694
138	−1.851	8.339	2.421	−118.508	−10.961	8.015	2.002	−182.9260137
139	−0.829	2.746	2.149	−86.832	−8.377	8.299	1.390	−182.8796575
153	−2.983	5.968	−13.341	−133.843	−12.099	38.143	9.659	−182.9227519
164	−34.434	25.624	10.023	−169.202	−18.846	4.459	0.119	−183.0402980
169	−1.851	8.529	0.966	−118.735	−7.570	8.356	1.611	−182.9230649
172	−0.172	0.057	4.447	−41.776	4.121	6.656	0.661	−182.7912930
191	−0.155	0.700	3.756	−59.686	−14.085	−4.153	0.873	−182.8657873
195	−0.654	2.593	−0.681	−86.852	0.506	−2.367	0.143	−182.8889914
200	−0.260	6.849	−8.465	−52.241	−22.059	−14.914	1.936	−182.8919270
201	−0.234	5.197	−13.531	−71.262	−15.217	−9.142	2.431	−182.9120130
202	−3.961	10.699	−19.467	−144.039	−1.558	1.300	4.106	−182.9935466
205	−0.024	2.651	−19.704	−54.539	−1.467	−4.069	1.646	−182.8701770
207	−18.099	1.612	28.348	−61.395	−47.456	−17.519	3.402	−182.9269126
210	−0.139	0.622	4.761	−46.584	−15.468	−11.035	0.759	−182.8567544
211	−0.215	1.201	2.452	−64.145	−9.785	−9.504	0.412	−182.8766779
212	−3.681	13.219	−1.102	−142.186	2.125	−6.574	−0.660	−182.9711405
217	−17.940	5.852	21.752	−68.827	−64.437	−22.828	7.337	−182.9715076
219	−26.217	14.033	6.276	−132.603	11.118	−1.807	2.773	−182.9513267
220	−0.333	1.471	−10.920	−50.189	−22.401	−4.683	3.639	−182.8827833
221	−0.218	1.001	−15.145	−60.003	−15.730	−1.321	3.532	−182.8899024
222	−0.556	1.792	−19.504	−92.802	−2.779	3.002	3.648	−182.9206843

The analysis of Table II (the classical decomposition of the total energy) is very simple. In cases 5, 13, and 18, the fluorine ion is at $x = -5.15$ a.u. and the lithium ion is at $x = +3.58$ a.u. from the oxygen (i.e., the configuration F–H_2O–Li), or at $x = -7.5$ a.u., or at $x = -15.0$ a.u. The two-body interaction for Li–F namely V(Li–F), and the remaining two-body interactions, V(Li–H_2O) and V(F–H_2O), are exactly as described previously.[1,3] The contribution $E(s, 3)$ is simply the difference between the total Hartree–Fock stabilization energy and the sum of the two-body terms. In case 5, the complex F–H_2O–Li is compact and the energy $E(s, 3)$ is found to be attractive and large (about −8.6 kcal/mole). In case 18, the Li–F–H_2O complex is very diffuse [R(Li–R) = 9.85 a.u. and R(F–O) = 5.15 a.u.] and $E(s, 3)$ is repulsive and small. We might expect these cases to be typical of Li^+–$(F–H_2O)^-$, but from the data available we cannot confirm this simple interpretation. Indeed, it is difficult to obtain much physical insight from this part of the table, and perhaps one can only conclude that $E(s, 3)$ is about 10% of $E(s, 2)$ for a complex which is compact, but tends to decrease the more the complex is separated either into three distant single bodies, or into a two-body pair with a distant third body.[15]

Let us now comment briefly on the BEA data presented in Table III. Firstly, we note that essentially all the three-body terms are positive (repulsive). Secondly, all the E(Li) terms are negative (attractive) and at times rather large. The largest value of E(Li) found corresponds to case 13 for the Li–F–H_2O complex. For *this case*, we are tempted to state that the −171.416 kcal/mole for E(Li) might suggest the process $Li^+ \rightarrow Li$, that the +60.872 kcal/mole for E(F) represents the process $F^- \rightarrow F$, and that the E(Li–F) of −43.224 kcal/mole represents the remaining interaction (the ionization energy for Li and the electron affinity for F are 124.3 kcal/mole and 70.8 kcal/mole, respectively). Unfortunately, we cannot confirm this supposition because, in case 13, the basis set of the component atoms of the complex overlap to an extent that the BEA is not too meaningful. (It is noted that in such cases the electron population analysis suffers from the same disease, but less so.) The main result that we can obtain from the data in Table III is an alternative viewpoint in the binding mech-

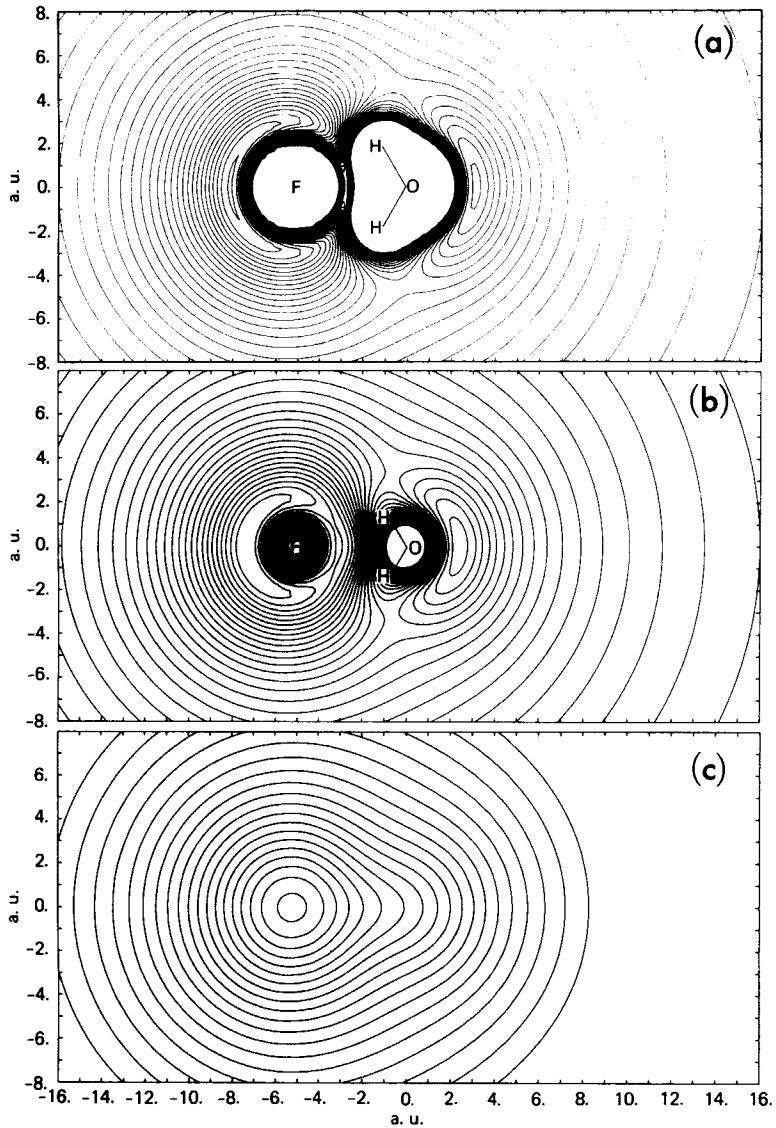

FIG. 7. Contour energy maps from the Hartree–Fock computation. The water molecule is fixed as indicated in Fig. 1. The fluorine nucleus is at $x = -5.15$ a.u. The lithium nucleus is in the xy plane at $z = 0.0$, 2.0, and 4.0 a.u. (top, middle, and bottom map, respectively). The contour interval is 5.0 kcal/mole. The corresponding two-body contour energy maps are given in Fig. 4. The qualitative features of the maps in Fig. 4 and in this figure are nearly the same, but not the quantitative features; for example, the number of contours around the secondary minimum in Fig. 4 is larger than the corresponding number of contours in this figure.

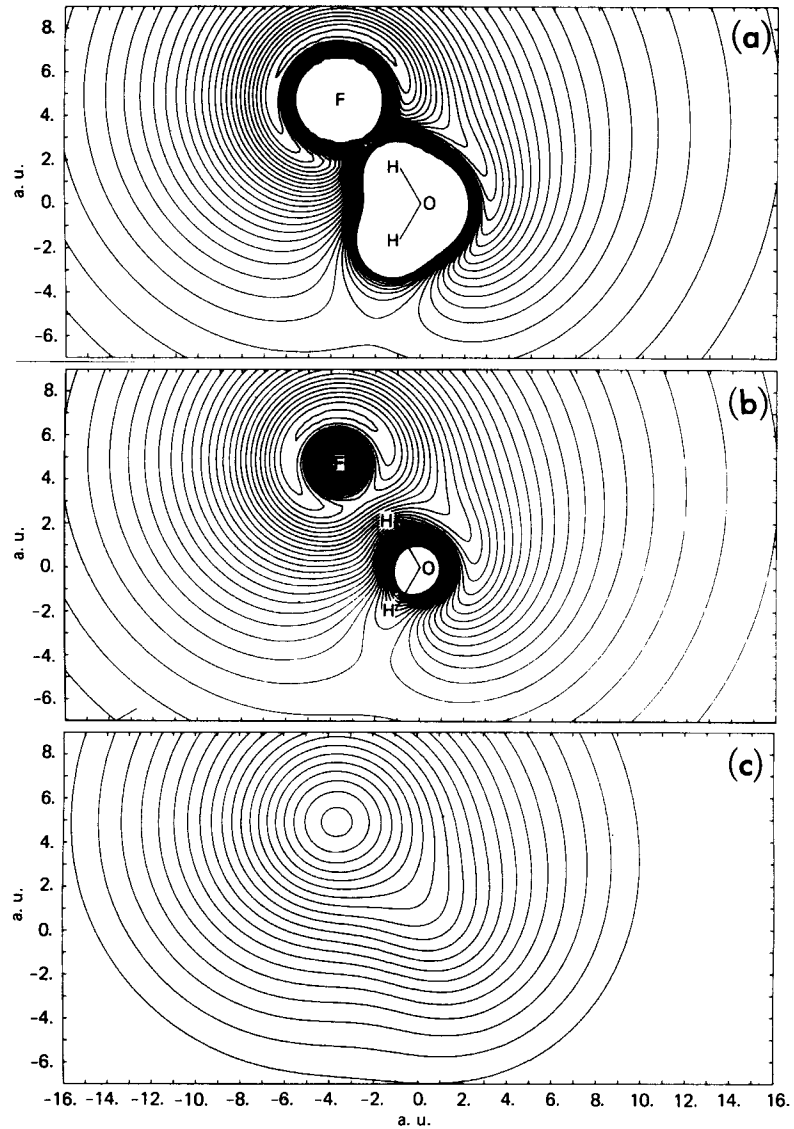

FIG. 8. Contour energy maps from the Hartree–Fock computation. The water molecule is fixed as indicated in Fig. 1. The fluorine nucleus is fixed in the hydrogen-bond position (see text). The lithium nucleus is on the xy plane at $z = 0.0$ a.u. (top map), or at $z = 2.0$ a.u. (middle map), or at $z = 4.0$ a.u. (bottom map). The contour interval is 5.0 kcal/mole. The corresponding two-body contour energy maps are given in Fig. 5.

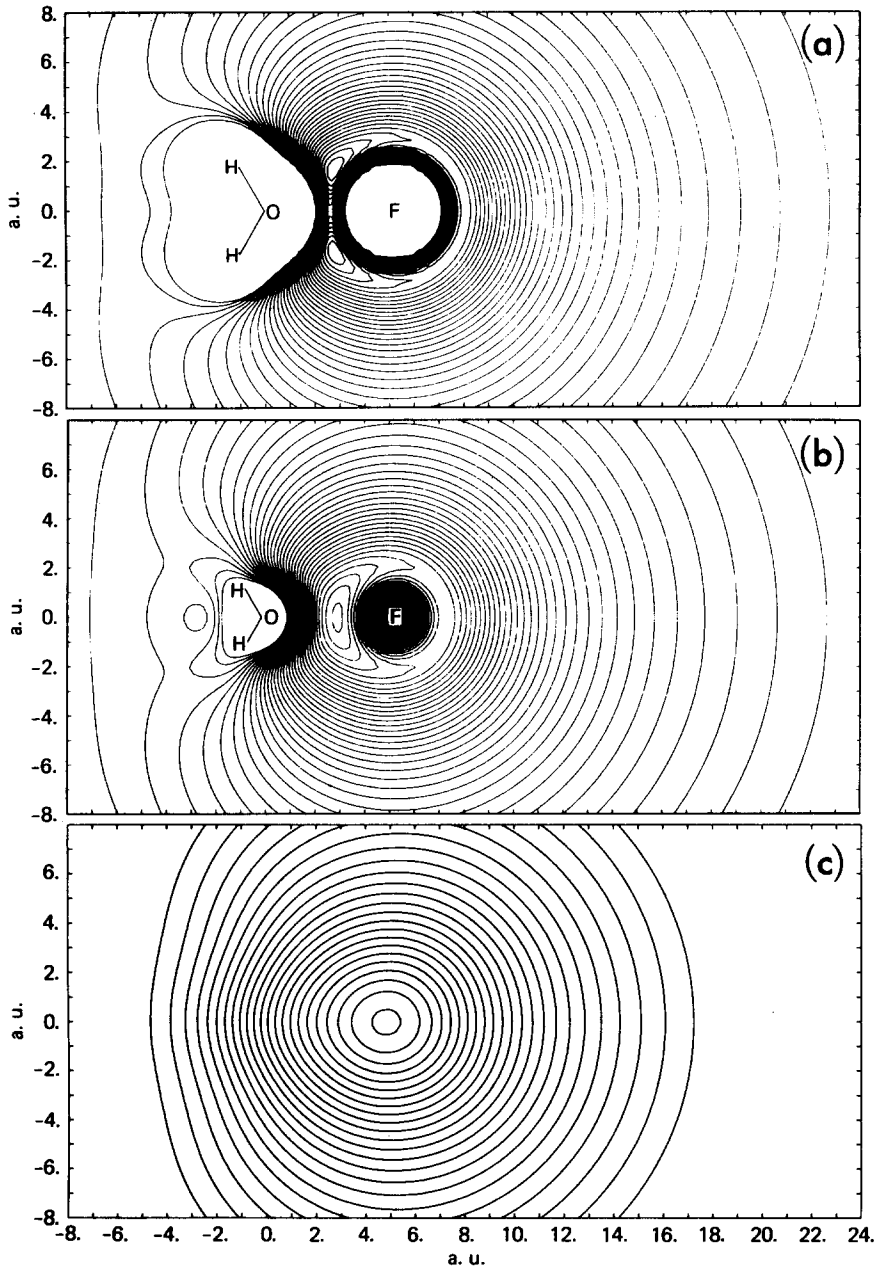

FIG. 9. Contour energy maps from the Hartree–Fock computation. The water molecule is fixed as indicated in Fig. 1. The fluorine nucleus is placed at $x = +5.15$ a.u. The lithium nucleus is either in the xy plane at $z = 0.0$ a.u., or in the xy plane at $z = 2.0$ a.u., or in the xy plane at $z = 4.0$ a.u., respectively, for the top, middle, and bottom maps. The contour interval is 5.0 kcal/mole. The corresponding two-body contour energy map is given in Fig. 6.

anism of the complex. Having noted that $E(s, 2)$ is not too different from $E(s, 2) + E(s, 3)$, one could deduce that the binding mechanism describing the 3 two bodies is essentially an adequate description for the binding mechanism of the three-body system. On the other hand, one might suspect that near an equilibrium geometry the total binding energy is the result of a complex mechanism, such as a cancellation of terms. This cancellation of terms seems to be suggested by the BEA data.

From a thorough analysis of the data presented in Table III, we cannot only conclude qualitatively that the assumption of pairwise addivity is only an approximation, but more importantly, we have provided numerical data on its limitation and/or validity. The extent of the polarization of (and hence energy changes in) one- and two-body systems when in the field of the full H_2O–Li–F

TABLE IV. Constants needed to fit the energy surface for the Li–F–H_2O complex.

	F	Li	LiF
Q	−0.53544971	0.54877581	
Q_m	−0.05638953	0.01021204	
A_1	0.02382738	8.62957004	
A_2	499.999935	119.999996	
a_3	1.15802317	3.12848282	
a_4	2.52354884	2.76618096	
b_1			−1.05672429
b_2			1.03197828
b_3			39.5052792
b_4			−2.36780241

$XR1 = -0.257415782$	$XM = -0.0308938$
$YR1 = 0.0$	$YM = 0.0$
$ZR1 = 0.001385405$	$ZM = 0.0$

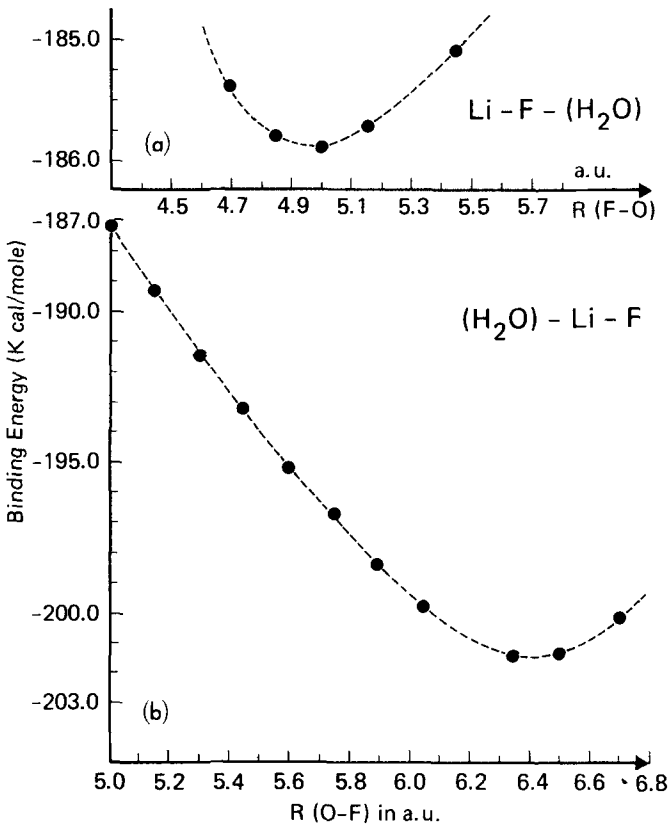

FIG. 10. Stabilization energy from the Hartree–Fock computation (in kcal/mole) for the Li–F–H_2O complex (top) and for the H_2O–Li–F complex (lower diagram) in the xy plane at $z = 0.0$ a.u. In the two cases F–O distance (or the O–F distance) is varied. The Li position for the most stable configuration can be obtained from the map.

complex can be appreciated by considering the energy-contour maps presented in Figs. 7, 8, and 9. These plots are similar to Figs. 4, 5, and 6, except that here we plot the total stabilization energy, i.e., we include $E(s, 3)$.[16] The interval between contours is again 5 kcal/mole. It should be stressed that an energy of 5 kcal/mole is a large number; therefore, a seemingly very small difference between contours on the map may correspond to significant chemical differences.[17]

In Fig. 7 the fluorine is positioned at $x = -5.15$ a.u., $y = z = 0.0$ a.u.; the lithium is constrained to the xy planes at $z = 0.0$ a.u., $z = 2.0$ a.u., and $z = 4.0$ a.u. The corresponding stabilization energies are -185.58 kcal/mole (-184.90 kcal/mole), -184.98 kcal/mole (-184.21 kcal/mole), and -161.46 kcal/mole (-160.46 kcal/mole); the value in parentheses corresponds to $E(s, 2)$ for the particular configuration.

In Figs. 8 and 9, the Li^+ ion is not restricted to the xy plane at $z = 0.0$ a.u.; rather, we consider xy planes situated at $z = 0.0$ a.u., $z = 2.0$ a.u., and $z = 4.0$ a.u. In Fig. 8, the hydrogen bonding case, the three planes ($z = 0.0$ a.u., $z = 2.0$ a.u., and $z = 4.0$ a.u.) accessible to the Li^+ ion are characterized by the following minimum values of the stabilization energy: -186.81 kcal/mole (-190.74 kcal/mole), -186.12 kcal/mole (-189.90 kcal/mole), and -161.63 kcal/mole (-165.00 kcal/mole), respectively.

In Fig. 9 the fluorine is placed at $x = 5.15$ a.u.; the corresponding stabilization energies are -185.58 kcal/mole (-185.58 kcal/mole), -184.98 kcal/mole (-184.89 kcal/mole), and -161.46 kcal/mole (-161.14 kcal/mole) for Li^+ in the xy plane at $z = 0.0$ a.u., $z = 2.0$ a.u., and $z = 4.0$ a.u.

In Fig. 10 we present the results of a series of calculations in which the F^- ion is moved progressively closer to the water molecule. For the Li–F–H_2O (C_{2v}) complex, the minimum in the stabilization energy (-185.7 kcal/mole) is obtained at an F–O distance of about 5.0 a.u. We also report in this figure the optimal stabilization energy for the H_2O–Li–F complex; the optimal O–F distance, about 6.42 a.u., corresponds to a stabilization energy of -201.4 kcal/mole.

In Figs. 11 and 12, we fix the Li^+ position in the xy plane at $z = 0.0$ a.u. In Fig. 11 we present the contour energy diagrams for the F^- ion at $x = -5.15$ a.u., $x = -5.0$ a.u., $x = -4.85$, and $x = -4.70$ a.u. In Fig. 12 we present the contour energy diagrams for the F^- ion at $x = 6.15$ a.u., $x = 6.35$ a.u., $x = 6.50$ a.u., and $x = 6.70$ a.u.

V. FITTING OF THE HARTREE-FOCK ENERGIES

As mentioned in the Introduction, the main goal of this work is to obtain a potential energy function that describes in a continuous way the energy of any configuration of the H_2O–Li–F system in which the F^- is contained within the H_2O plane. This potential will be used as the starting point in statistical-mechanical studies of the properties of aqueous lithium fluoride solutions.

Our potential energy expression has the following form:

$$+ Q^{F}[(R(H_1, F))^{-1} + (R(H_2, F))^{-1} - (R(F, R_1))^{-1} - (R(F, R_2))^{-1}] - Q_{m}^{F}[(R(M_1, F))^{-1} + (R(M_2, F))^{-1} - 2(R(F, O))^{-1}]$$

$$+ A_1^{F}[\exp(-a_3^{F} R(H_1, F)) + \exp(-a_3^{F}(R(H_2, F))] + A_2^{F}[\exp(-a_4^{F} R(F, M))]$$

$$+ Q^{Li}[(R(H_1, Li))^{-1} + (R(H_2, Li))^{-1} - (R(Li, R_1))^{-1} - (R(Li, R_2))^{-1}]$$

$$- Q_{m}^{Li}[(R(M_1, Li))^{-1} + (R(M_2, Li))^{-1} - 2(R(Li, O))^{-1}] + A_1^{Li}[\exp(-a_3^{Li} R(H_1, Li)) + \exp(-a_3^{Li} R(H_2, Li))]$$

$$+ A_2^{Li}[\exp(-a_4^{Li} R(Li, M))] + b_1 R(Li, F)^{-1} + b_2 R(Li, FO^{-3} + b_3 \exp(b_4 R(Li-F)) .$$

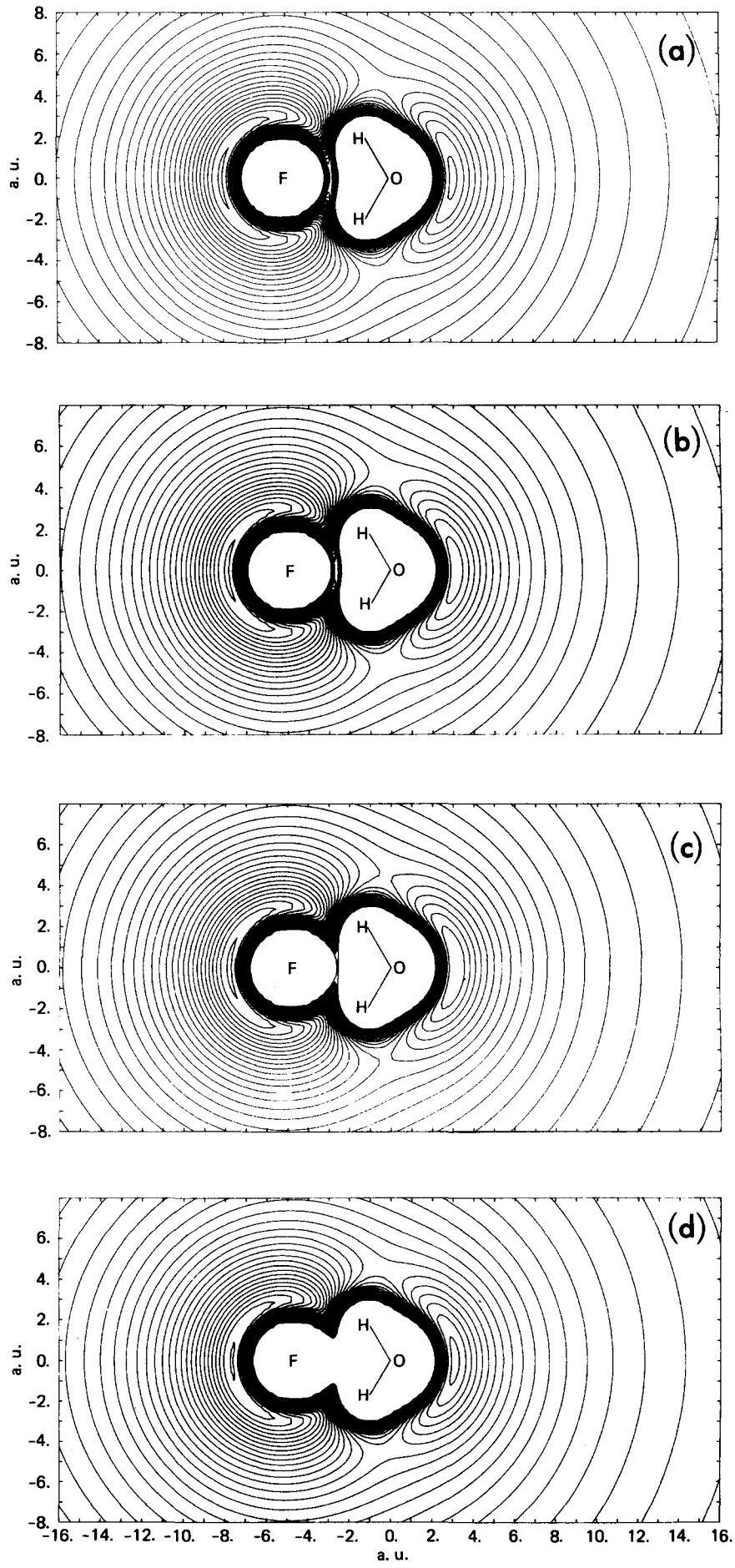

FIG. 11. Contour energy maps for the Li–F–H_2O complex in the Hartree–Fock approximation. The water molecule is fixed as indicated in Fig. 1. The fluorine nucleus position is at $x=-5.15$ a.u. (top map), at $x=-5.00$ a.u. (second map from the top), $x=-4.85$ a.u. (second map from the bottom), and at $x=-4.70$ a.u. (bottom map). The lithium ion positions at the minimum energy are visible from the maps at the left of fluorine and at the right of the water molecule. The contour interval is 5.0 kcal/mole. The dark areas surrounding the fluorine and water are the result of nearly overlapping repulsive contours defining the hard core (the repulsive contours given up to ~20 eV) above dissociation energy into F^-, Li^+, and H_2O.

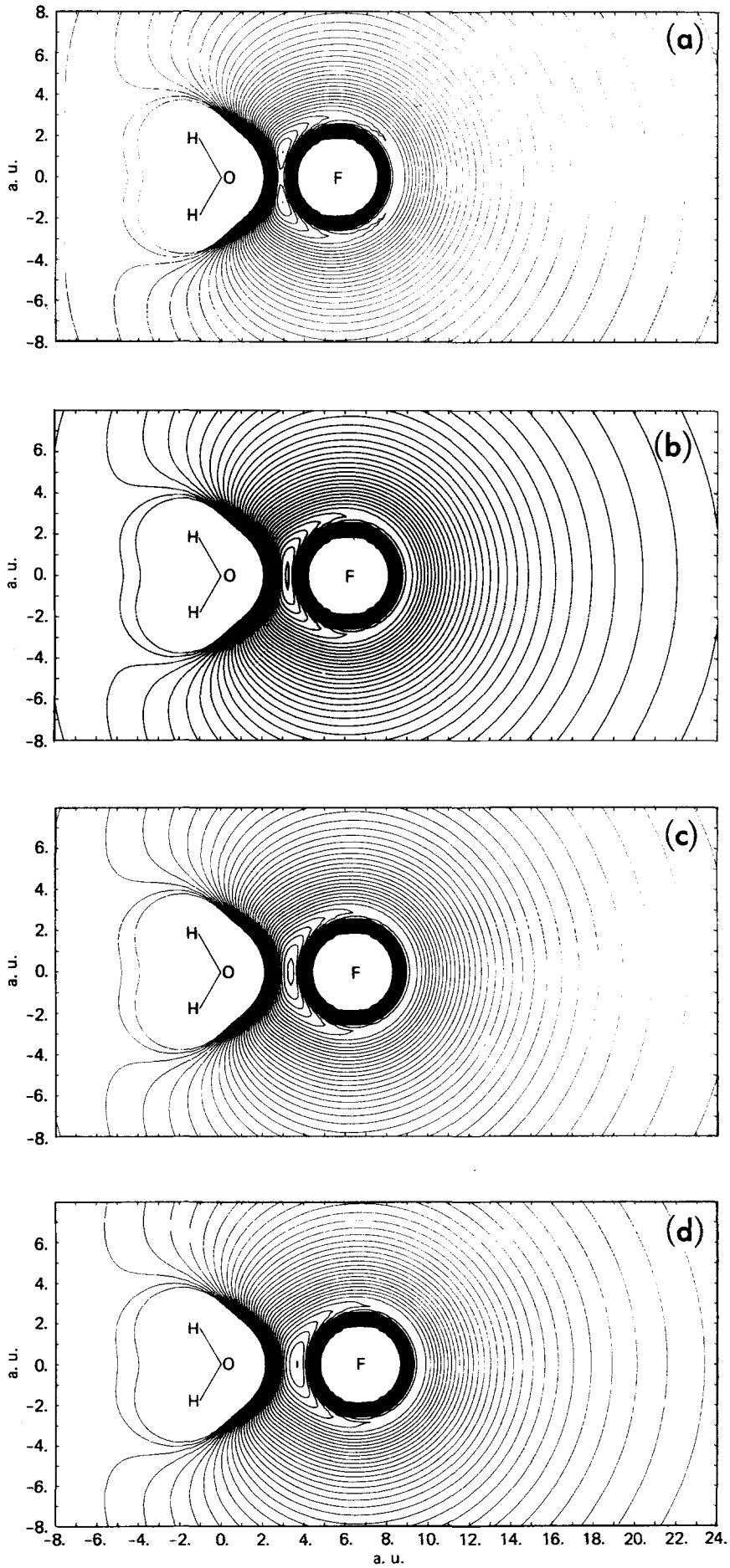

FIG. 12. Contour energy maps for the H_2O–Li–F complex in the Hartree–Fock approximation. The water molecule is fixed as indicated in Fig. 1. The positions for the fluorine nucleus are $x = 6.15$ a.u., $x = 6.35$ a.u., $x = 6.50$ a.u., and $x = 6.70$ a.u., respectively (for the top and bottom maps). The contour interval is 5.0 kcal/mole. The minimum (or minima for case a) are between the fluorine and the oxygen. The dark area results from the near superposition of many contour lines, delimiting the hard core repulsive part. For graphical reasons such contours are not given when the last repulsive contour is ~ 20 eV above the energy for the Li^+, F^-, H_2O dissociation products.

The definitions of the variables $R1$, $R2$, $M1$, $M2$, and M can be found in Ref. 4. The potential was fitted until the standard deviation obtained by including the 250 computed points (corresponding to about 600 geometrical configurations when symmetry is taken into account) was of the order of 0.00020 a.u. The values of the constants obtained from the fitting of the potential function are found in Table IV. In this table, the $XR1$, $YR1$, $ZR1$, XM, YM, ZM refer to the Cartesian coordinates (in a.u.) for the species $R1$ and M.

VI. CONCLUSIONS

By presenting the potential for the H_2O–Li–F complex, and by having reported[7–9] that quantum-mechanically derived potentials (such as the one discussed in this work) yield structural information comparable in accuracy to the latest neutron diffraction data, we have demonstrated that the theory of liquids, clusters, and solutions has entered the stage of accurate quantitative predictions.

We note that each computed point of Table II costs about 15 min of computer time on an IBM 360/195 computer. Thus, the type of work here presented is not the result of exceptional computational facilities, but rather the consequence of progress of computational techniques.[11]

The potential derived in this work is now being used to determine the structure of the Li–F aqueous solution,[18] using statistical mechanics; in parallel, we are determining the structure using the two-body potentials previously reported.[14] A comparison of the structures will quantitatively assess the limitations of the pairwise-additivity approximation.

APPENDIX

In this Appendix, we specify the Gaussian basis set for the lithium ion, the fluoride ion, and the water molecule.

TABLE A. I. Gaussian basis set for Li^+ ion.

Contracted function	Type	Orbital exponent	Contraction coefficient
1	S	0.027778	1.000000
2	S	0.074659	1.000000
3	S	0.338768	1.000000
4	S	0.704648	1.000000
5	S	1.629590	1.000000
6	S	4.084140	0.268080
6	S	11.061900	0.124590
7	S	33.377100	0.041710
7	S	116.989000	0.010630
7	S	513.280000	0.002060
7	S	3427.560000	0.000270
8,9,10	X, Y, Z	0.028220	1.000000
11,12,13	X, Y, Z	0.100680	1.000000
14,15,16	X, Y, Z	0.450620	1.000000

TABLE A. II. Gaussian basis set for F^- ion.

Contracted function	Type	Orbital exponent	Contraction coefficient
1	S	0.120891	1.000000
2	S	0.414699	1.000000
3	S	1.292400	1.000000
4	S	3.958260	1.000000
5	S	8.711330	0.461521
5	S	19.622100	0.567770
6	S	46.659100	0.714299
6	S	119.039000	0.318572
7	S	330.641000	0.783108
7	S	1021.770000	0.222784
7	S	3646.290000	0.052752
7	S	16201.000000	0.009910
7	S	109236.000000	0.001061
8,12,16	X,Y,Z	0.108562	1.000000
9,13,17	X,Y,Z	0.367845	1.000000
10,14,18	X,Y,Z	1.045840	0.637085
10,14,18	X,Y,Z	2.731420	0.426778
11,15,19	X,Y,Z	7.096300	0.797789
11,15,19	X,Y,Z	19.852100	0.232757
11,15,19	X,Y,Z	63.754300	0.046834
11,15,19	X,Y,Z	273.820000	0.005521
20,21,22	XX,XY,XZ	2.000000	1.000000
23,24,25	YY,YZ,ZZ	2.000000	1.000000

TABLE A. III. Gaussian basis set for H_2O.

Center	Contracted function	Type	Orbital exponent	Contraction coefficient
O	1	S	0.22054	1.000000
O	2	S	0.60550	0.542847
	2	S	1.538730	0.184333
O	3	S	5.386180	0.282798
	3	S	13.617900	0.423426
O	4	S	35.460900	0.269411
	4	S	98.515300	0.110308
	4	S	301.426000	0.034182
	4	S	1062.620000	0.008449
	4	S	4669.380000	0.001627
	4	S	31195.600000	0.000209
O	5,8,11	X,Y,Z	0.150740	1.000000
O	6,9,12	X,Y,Z	0.423600	0.327403
	6,9,12	X,Y,Z	1.128480	0.308806
O	7,10,13	X,Y,Z	2.972370	0.169262
	7,10,13	X,Y,Z	8.320770	0.062925
	7,10,13	X,Y,Z	26.876700	0.014055
	7,10,13	X,Y,Z	114.863000	0.001892
O	14,15,16	XX,XY,XZ	1.000000	1.000000
O	17,18,19	YY,YZ,ZZ	1.000000	1.000000
H1,H2	20,25	S	0.089859	0.048364
	20,25	S	0.258165	0.134580
H1,H2	21,26	S	0.798266	0.179965
	21,26	S	2.825680	0.042371
	21,26	S	12.418500	0.010282
	21,26	S	82.702800	0.001256
H1,H2	22,27	X	0.750000	1.000000
	23,28	Y	0.750000	1.000000
	24,29	Z	0.750000	1.000000

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[15]Note: We can be more specific. The value of $E(s,3)$ is attractive (−10 kcal/mole) for an optimal Li−(H_2O)−F geometry, repulsive (+5 kcal/mole) for an optimal Li−F−(H_2O) or (H_2O)−Li−F geometry; the charge transfer (internal) in the H_2O molecule and the permanent dipole moment are affected by the ionic charge [see, for example, E. Clementi and D. Klint, J. Chem. Phys. 50, 4899 (1969) and E. Clementi, J. Chem. Phys. 54, 2492 (1971) for a discussion of point charge perturbation on molecules, computed in the Hartree−Fock approximation].
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[17]In Ref. 7, we have concluded that much of the structure in the correlation function g_{O-O} for liquid water is due to three-body effects, for distances larger than about 4 Å.
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