Electrostatic Interactions in Host-Guest Complexes 2

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In this article the quantum chemically calculated charge density distribution of 18-crown-6 and the $K^+ \ldots$ 18-crown-6 complex are compared with the charge density distribution of smaller molecules and corresponding complexes which can be considered as fragments of the 18-crown-6 molecule. An analysis of the charge density distribution in terms of atomic charge distribution according to the stockholder recipe gives accurate rules for the transferability of the charge density distribution. This gives us the possibility to construct the charge density distribution of large molecules out of accurate large basis set results on small molecules.

INTRODUCTION

The well-known crown ether compounds derive their complexing ability mainly from their shape and inhomogeneous electron distribution. To describe the electrostatic interactions of these compounds with their guest molecules a detailed description of the electron density distribution is needed. Unfortunately the size of the molecules make *ab initio* calculations of the electronic structure of the molecular complexes very difficult. The problem is aggravated by the requirement of the use of large basis sets to give a satisfactory description of the free host molecule and of the polarized molecule in the complex. The present study concentrates on model studies to verify the use of the electron density distribution of small molecules to describe the electron density in large crown ether compounds.

In the first article in this series,[1] further referred as article I, we presented an analysis of the intermolecular interaction in the $K^+ \ldots H_2O$ complex as a model system for the $K^+ \ldots$ 18-crown-6 complex. In this article a series of HFS calculations on larger fragments of the 18-crown-6 $\ldots K^+$ complex are presented. The electron density distribution is analyzed in terms of atomic charges and multipoles so as to describe the electrostatic interactions between the host and the guest molecule. The results are compared with a calculation on the complex itself. Owing to the high symmetry (D_{3d}) that can be assigned to the complex, it can be handled by the HFS-method using a large basis set.

Unfortunately the HFS-method does not yield reliable values for binding energies due to a poor representation of the exchange hole near the nu-clei.[2] Therefore the results are restricted to electrostatic interaction which can be derived from the electron density distribution. The HFS method has given very accurate results in electron density studies of oxalic acid dihydrate.[3] Dipole moment and polarizabilities of water have been calculated by this method, which are very close to the experimental values.[4] Several theoretical studies on crown ether complexes[5,6] did appear in literature. These studies are restricted to STO-3G level. Owing to the low quality of the basis set the polarization effects are strongly underestimated and the charge transfer overestimated.

Starting with the $K^+ \ldots H_2O$ complex the fragment is subsequently enlarged in small steps so as to resemble more and more the 18-crown-6 $\ldots K^+$ complex. The electron density distribution of the complexes $H_2O \ldots K^+$, $CH_3OH \ldots K^+$, $CH_3CH_2OH \ldots K^+$, $CH_3OCH_3 \ldots K^+$, and the free molecules are expressed in atomic charges and dipole moments. Polarization effects of complexation are observed and can be compared with the ones in the 18-crown-6 $\ldots K^+$ complex. Parameterizations of the charge distribution of H_2O, CH_3OH and CH_3OCH_3 in terms of atomic charges have been published by several authors.[7-10] These atomic charges have been obtained by Mulliken charge partitioning, or are chosen so as to reproduce either the electrostatic potential outside the van der Waals radius, or the molecular multipoles. The values calculated by these various methods differ considerably yielding charges for the oxygen atom in H_2O that vary from $-.37$ to $-.99$ e. Moreover atomic charges obtained in these ways do not seem to be transferable. The parameters that describe the CH_3 groups in dimethyl ether and in methanol are totally different, although

the groups are chemically very similar. In this work we define atomic charge distributions using Hirshfeld's stockholder method.[11] Subsequently these strictly local charge distributions are characterized by charge and dipole moment. With this detailed analysis we hope to get better insight in the possibilities and the limits of the transferability of atomic charge parameters. The stockholder method is an alternative to Baders method of "atoms in molecules."[12] The latter method has a profound basis in quantum mechanics. The disadvantages are the heavy demands on computational facilities and the fact that it does not indicate the shift of charge with respect to the promolecule.[13] The stockholder method results in a partitioning of the molecule in atoms, the seizes of which are related to the free atomic radii. It has the advantage that the structure factors of the fragments make sense. The method can be applied to *ab initio* calculated molecular electron densities, as well as to experimental X-ray electron density distributions.

COMPUTATIONAL METHODS

HFS-LCAO-DVM

In our calculations we employed the $X\alpha$-LCAO-DVM version of the density functional method. In the spin restricted case, the density functional method, as defined by the Hohenberg–Kohn–Sham formalism,[14,15], entails the self-consistent solution of

$$[-1/2\nabla^2(1) + V_{\text{eff}}(1)]\varphi_i(1) = \varepsilon_i\varphi_i(1) \qquad (1)$$

where

$$V_{\text{eff}}(1) = -\sum \frac{Z_n}{r_{1n}} + \int \frac{\rho(2)}{r_{12}}d^3r_2 + V_{XC} \qquad (2)$$

In the $X\alpha$-version, the exchange-correlation potentials V_{XC} is approached by the expression

$$V_{XC} = -3\alpha\left[\frac{3\rho(1)}{8\pi}\right]^{1/3} \qquad (3)$$

where α is an adjustable parameter taken to be 0.7 throughout the present work.

In the $X\alpha$-LCAO-DVM version as developed by Baerends, Ellis, and Ross,[16] one-electron orbitals are expanded in a finite basis set of Slater-type functions centered on the atomic nuclei. To overcome the fact that the number of integrals to be evaluated increases as n^4, if n is the number of basis functions, the discrete variational method (DVM)[17] was used, which enables us to use extended basis sets, without making the problem intractable.

Stockholder Recipe

The stockholder recipe[11] is a method to divide the total electron density distribution of a molecular system into overlapping atomic parts.

$$\rho(r) = \sum \rho_i(r) \quad (1) \qquad (4)$$

The atomic electron densities are defined by

$$\rho_i(r) = w_i(r)\rho(r) \qquad (5)$$

The weight factor $w_i(r)$ is based on the promolecule electron density distribution, which is defined as the sum of the spherical averaged densities of the free atoms.

$$\rho_{pm}(r) = \sum \rho_i^{\text{free}}(r) \qquad (6)$$

The weight factor $w_i(r)$ is now defined as

$$w_i(r) = \frac{\rho_i^{\text{free}}(r)}{\rho_{pm}(r)} \qquad (7)$$

The atomic charges and dipole moments are calculated by integration of the stockholder atomic densities. The origins for the atomic dipole moments are the nuclear centers.

$$q_i = \int \rho_i(r)d^3r - Z_i \qquad (8)$$

$$\mu_i = \int (r - R_i)\rho_i(r)d^3r \qquad (9)$$

The integration is carried out by Gauss quadrature in polar coordinates, with the origin on the atom in consideration. The radius is divided in several intervals and in each of them Gauss–Legendre points are used. In the angular coordinates, Gauss–Legendre is used for $\cos(\vartheta)$ and a regular grid for ϕ. This way of integration gives a better result than a regular grid in Cartesian coordinates. The numerically calculated total charge of the $K^+ \ldots$ 18-crown-6 complex is 1.004 which illustrates the accuracy of the integration. The spherical averaged atomic densities are taken from HF-data.[18] The atomic charges according to (5) are not as basis set dependent as Mulliken charges. The charges and dipole moments of the atoms yield charge and dipole moment of the molecule. The basis sets we used for calculating the atomic charges and dipole moments are given in Table I. For the water complex we used the basis set of I.

CALCULATIONS AND RESULTS

Geometry of the Complexes

Figure 1 shows the geometry of the $K^+ \ldots$ 18-crown-6 complex in the D_{3d} conformation. The

Table I. Basis sets. In all calculations the 1s-shell of the non-hydrogen atoms was kept frozen. For the valence shells the following Slater type basis sets were used.

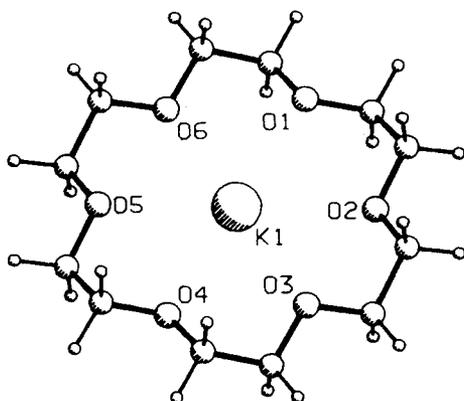| O(dzd)		C(dzd)		H(dzp)		K^+(tzd)	
1s	7.36	1s	5.40	1s	0.76	1s	18.42000
2s	1.70	2s	1.24	1s	1.28	2s	7.30079
2s	2.82	2s	1.98	2p	1.00	2s	16.70010
2p	1.30	2p	0.96			3s	3.88331
2p	3.06	2p	2.20			3s	2.40881
3d	2.00	3d	2.50			3s	5.70995
						2p	15.19580
						2p	8.61735
						3p	3.24817
						3p	1.94563
						3p	6.88378
						3d	2.14000

Figure 1. Geometry of K^+ ... 18-crown-6
C—O = 1.418Å C—H = 1.090Å C—O—C = 112.2°
C—C = 1.504Å O—K = 2.789Å C—C—O = 108.5°

oxygen atoms are nearly coplanar. Half of the C—H bonds are about perpendicular, the other half about parallel to this plane. The geometry of the K^+ ... H_2O complex is the one of article I. The interatomic distances and bond angles of the other fragments are chosen so as to be the same as the corresponding distances and angles in the K^+ ... 18-crown-6 complex. In Table II the dipole moments of the fragments calculated from the HFS wave functions are compared with experimental values. The dipole moment of H_2O is reproduced very accurately. The dipole moments of methanol and dimethyl ether differ with the experimental values, partly due to the fact that we did not use the experimental geometries but the

18-crown-6 fragment geometry and partly due to the use of a smaller basis set than for water.

Atomic Charge Distribution in 18-Crown-6 and Fragments

In this section we present results of HFS calculations on 18-crown-6 and on fragments of this molecule saturated with hydrogen atoms. The charge distributions of the free molecules are partitioned by the stockholder recipe and the results are presented in Figure 2. This figure shows how the electron density distributions of the atoms are deformed by the chemical bonds. In the plots of the oxygen atom of water methanol and ethanol the same features in the region of the OH bond can be discerned. Similar transferable deformations of the atomic electron density distributions in bonding regions are shown for the other bonds. However, the plots show only the electron density distribution in the interatomic region, and do not inform about the diffuse regions of the electron density distributions; these are better described by the moments of the charge distributions. So in addition we calculated the total charge and the dipole moments of the atoms in the various molecules. Since the atoms are charged, it is necessary to define the origin in order to calculate the dipole moment. In all cases the value with respect to the nuclear position is reported. The results, presented in Figure 3, are discussed below.

The smallest molecule serving as a 18-crown-6 fragment is the water molecule. The free water molecule shows a strong negative charge on the oxygen atom of −.309 e and a positive charge on the hydrogen atoms of .154 e each. This only partly accounts for the well-known dipole moment of this molecule. The electrons in the oxygen atom move to the lone pair region resulting in an atomic dipole moment directed along the bisector of the H—O—H angle. As expected the atomic dipole moments of the hydrogens are directed along the O—H bond and point away from the oxygen atom. The contribution to the molecular dipole moment by the atomic charges has the same direction and about the same magnitude as the sum of the atomic dipole moments. Figure 3 shows the hydrogen atoms to be responsible for the major part of this sum.

Table II. Molecular dipole moments (Debye).

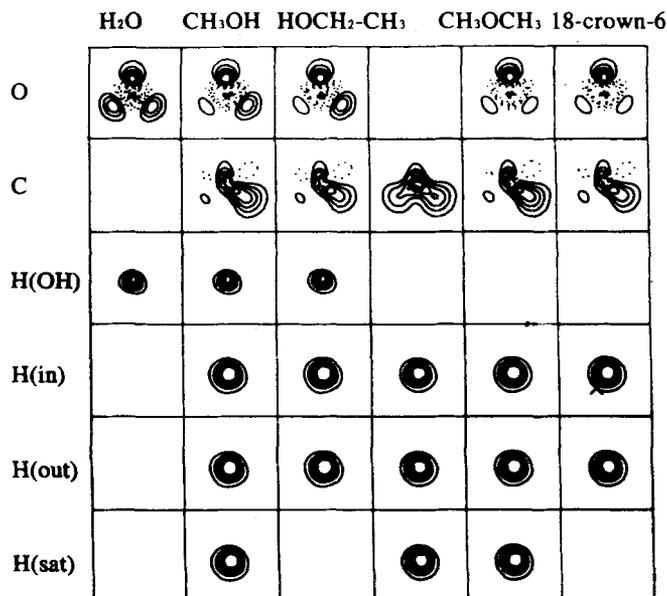|	Experimental	Calculated	Difference (%)
H_2O	1.85[19]	1.85	0
CH_3OH	1.70[20]	1.52	−11
CH_3CH_2OH	1.69[19]	1.23	−27
CH_3OCH_3	1.30[19]	1.13	−13

H₂O   CH₃OH   HOCH₂-CH₃   CH₃OCH₃ 18-crown-6

Figure 2. Contour plots of stockholder atomic electron density distributions. Depicted are the difference of the stockholder and the spherical averaged atomic electron distributions. Oxygen: H — O — H plane; carbon: O — C — H, O — C — C plane; hydrogen: H — O — H, H — O — C, H — C — H plane. Contour interval: 0.015 a.u., —positive contours, ... negative contours.

The second fragment we consider is methanol. Replacing a hydrogen atom of a water molecule by a CH₃-group has a large effect on the charge distribution. The oxygen atom in free methanol is less negative then the water oxygen. The transfer of charge between neighboring hydrogen and oxygen atoms is about the same in water and in methanol: .154 and .161 e. The charge transfer within the CH₃-group is much less, but not vanishing, leaving positive hydrogen atoms. A part of the electronic charge from the hydrogen atoms is passed on to the oxygen atom: .079 e, being much smaller than the charge transfer from the OH-hydrogen. The atomic dipole moment of the oxygen atom lies in the H — O — C plane, making an angle of 31.8° with the O — C bond. This suggests that the oxygen lone pair distribution slightly turns to the hydrogen region. The carbon dipole moment points to the oxygen atom. The dipole moment of the OH hydrogen atom points away from the oxygen atom, as was seen in the water molecule. The same holds for the CH₃-hydrogens: their dipole moments are directed along the C — H bonds, pointing away from the carbon atom, thus enforcing the dipole moment due to charge transfer.

The next fragment to discuss is dimethyl ether. The CH₃ groups in dimethyl ether act in the same way as the CH₃ group of methanol. The atomic charges and dipole moments and the polarization effects on complexation with K⁺ in the CH₃ group are about the same for both compounds. So the OH group in methanol and the remaining CH₃ group in dimethyl ether have only a minor effect on the CH₃ group. The contribution of the CH₃ group to the oxygen charge is also transferable: both in dimethyl ether and in methanol the oxygen atom gets −.080 e from the CH₃ group. The oxygen dipole moment in dimethyl ether is directed along the bisector of the C — O — C angle as in water.

The fourth fragment to consider is CH₃CH₂OH. The CH₃ group now is bonded to a carbon atom. This feature gives rise to a different charge distribution in the CH₃ group than in the CH₃OH and CH₃OCH₃ fragments. Since in 18-crown-6 all the carbon atoms are bonded to an oxygen atom, the charge distribution in the CH₃CH₂OH fragment will be of less use in predicting the charge distribution in 18-crown-6.

The last compound to be discussed is 18-crown-6 itself. The previous cases suggest that the atomic charges in the molecules are mainly determined by the hydrogen atoms which invariably donate electrons to the rest of the system. In 18-crown-6 there are relatively few hydrogen atoms, so the atomic charges on the carbon and oxygen atoms are expected to be lower than the ones in previously discussed molecules. This expectation is born out by the results of the calculation on 18-crown-6. The atomic dipole moments in 18-crown-6 are of the same magnitude and relative direction as the corresponding ones in dimethyl ether.
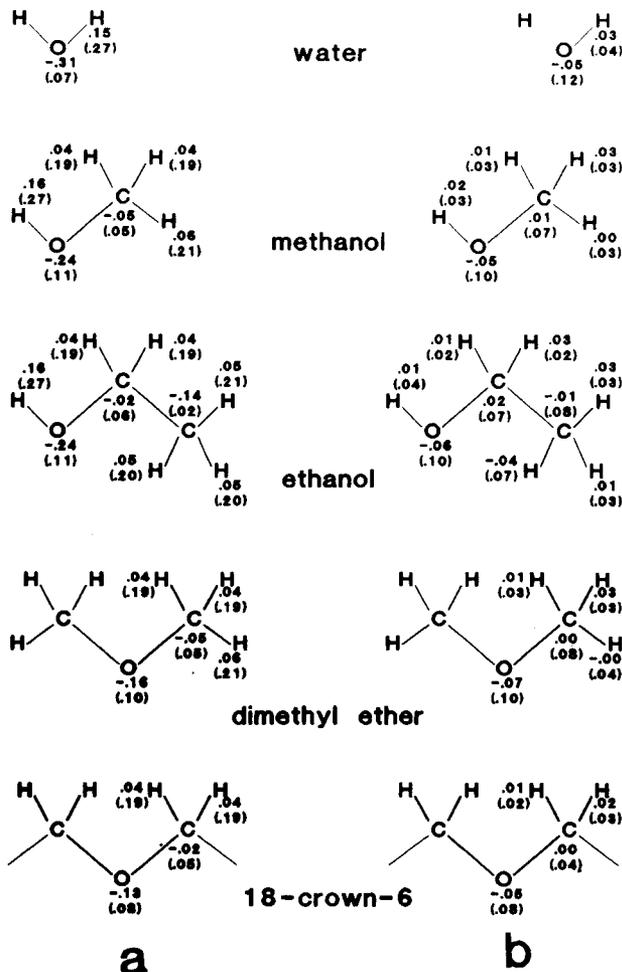
Figure 3. Atomic charges and dipole moments (in parentheses) of the host molecules (a) and the effect of complexation with K^+ (b). All quantities are given in a.u.'s.

EFFECT OF POLARIZATION

In its K^+ complex the water molecule is polarized by the cation. Charge flows from the hydrogens to the oxygen, the oxygen becoming more negative by an amount of $-.05$ e. On both the oxygen and the hydrogen atoms dipole moments are induced pointing away from the K^+ cation, thereby increasing the atomic dipole moments. Figure 3(b) shows that polarization of the oxygen atom adds .12 au to the total dipole moment. Each of the hydrogen atoms contribute .04 au. Charge transfer from the hydrogen atoms to the oxygen adds another .07 au., so as to make a total induced dipole moment of .27 au. The charge on the K^+ cation is .99 e, suggesting a charge transfer of .01 electron from the water to the K^+ cation. This is another example of the rule that the division between polarization and charge transfer is an arbitrary affair; it depends on the chosen boundaries of the atoms.

In its K^+ complex methanol shows polarization effects which are similar to those in the

$K^+ \ldots H_2O$ complex. Again on all atoms dipole moments are induced pointing way from the K^+ site. In water and methanol the induced atomic dipole moments on corresponding atoms are very similar and the charge transfer to the oxygen atom due to polarization by K^+ has about the same magnitude, with the charge transfer from the OH-hydrogen atom to the oxygen atom in methanol being slightly smaller than in the water complex. In ethanol and dimethylether the influence of the K^+-cation on the various atoms is seen to be similar to the corresponding ones in the compounds discussed above. The main difference is in the hydrogen atom at the site of the oxygen atom in the parent 18-crown-6 molecule. This hydrogen atom points to the K^+-cation with a much shorter K^+-H distance than in the other fragments. The effects of complexation of 18-crown-6 with the K^+ cation are in full accord with the results obtained above.

MODELING THE CHARGE DISTRIBUTIONS

On comparing 18-crown-6 and its fragments one observes that many charge distribution characteristics are transferable: hydrogen charges and dipole moments in both OH- and equivalent CH-groups do not differ much in these molecules. Hydrogen atomic charges in $C-CH_3$ groups are 0.05 e, in $O-CH_3$ $O-CH_2-C$ groups 0.04 e and in C-O-H groups 0.16 e. The effects of the field of the K^+ cation on the atomic charges and dipole moments are also transferable. From Figure 2 we see that this transferability is based on a detailed similarity of the charge distribution of the atoms when bonded to similar groups. The influence of the chemical environment also explains why the atomic charges on oxygen and carbon atoms in the various molecules differ. It is possible to correlate the atomic charges and dipole moments on the oxygen atoms to their chemical environment. The oxygen charge q_o is seen to depend on the number of hydrogens n_o bonded to the oxygen atom and to the number of hydrogens n_c bonded to neighboring carbon atoms. The following expression for the oxygen charge, expressed in atomic units, accounts for this charge.

$$q_o = -.157 * n_o - .029 * n_o \qquad (10)$$

The rather deviating value for the oxygen atoms of 18-crown-6 can be brought in line when the following expression is used.

$$q_o = -.119 * n_o - .014 * n_o - .075 \qquad (11)$$

In Table III the fitted oxygen charges are compared with the 'real' stockholder oxygen charges. The transferability of O and H charges implies

Table III. Comparison of stockholder charges and fitted charges on oxygen.[a]

	n_o	n_c	q_1 (e)	q_2 (e)	Δ_2 (%)	q_3 (e)	Δ_3 (%)
H_2O	2	0	−0.309	−0.314	1.9	−0.314	1.5
CH_3OH	1	3	−0.240	−0.244	1.5	−0.237	−1.0
CH_3CH_2OH	1	2	−0.230	−0.215	−6.6	−0.223	−3.0
CH_3OCH_3	0	6	−0.160	0.173	7.8	−0.161	0.8
18-crown-6	0	4	−0.129	−0.115	−11.	−0.129	−2.7

[a] q_1: stockholder charge, $q_2 = -0.157*n_o - 0.029*n_c$, $q_3 = -0.119*n_o - 0.014*n_c - 0.075$, Δ_2: $q_2 - q_1$, Δ_3: $q_3 - q_1$.

that the carbon charges are not, in general, transferable but are determined by electroneutrality.

The dipole moments of the oxygen atoms can be expressed as the sum of dipole moments along the bonds. By a least square fit two types of bond dipole moments are obtained, one along the OC — bond and one along the OH — bond. This gives the following values:

$$\mu_{OH} = .0544 \text{ a.u.}$$

$$\mu_{OC} = .0960 \text{ a.u.}$$

In Table IV the fitted dipole moments are compared with the 'real' stockholder dipole moments. From this table it follows that there is only a mi-

Table IV. Comparison of fitted and stockholder atomic dipole moments on oxygen.[a]

	μ_1 (a.u.)	μ_2 (a.u.)	Δ (%)	Angle
H_2O	.070	.066	−5	0.0°
CH_3OH	.114	.091	−20	2.0°
CH_3CH_2OH	.106	.091	−14	4.5°
CH_3OCH_3	.104	.107	3	0.5°
18-crown-6	.076	.107	40	9.2°

[a] μ_1: stockholder dipole moment, μ_2: fitted dipole moment, angle: angle between fitted and stockholder dipole moment.

nor contribution to the oxygen dipole moment from nonneighboring atoms. The direction of the oxygen dipole moment is very well reproduced by the fit. For the carbon atomic dipole moments this procedure does not make sense since the near tetrahedral symmetry does not allow an accurate derivation of bond dipoles from the total dipole moment.

In 18-crown-6 the charge transfer between the atoms, which determines the atomic charges and dipole moments, is influenced by the electrostatic field of the whole crown ether ring. A calculation of dimethyl ether in which the electrostatic field of the crown ether ring was simulated by the potential of the atomic charges and dipole moments of 18-crown-6 however showed a very small influence of the field of the ring on the charge distribution. So the differences of the charge distribution in dimethyl ether and 18-crown-6 are mainly determined by short range effects due to different chemical bonds.

The transferability of the atomic electron density distributions gives us the possibility to construct a contour map of the charge density distribution of 18-crown-6 out of the fragment atomic densities. This is illustrated in Figure 4, in which constructed maps are compared with maps calculated out of the 18-crown-6 wave func-
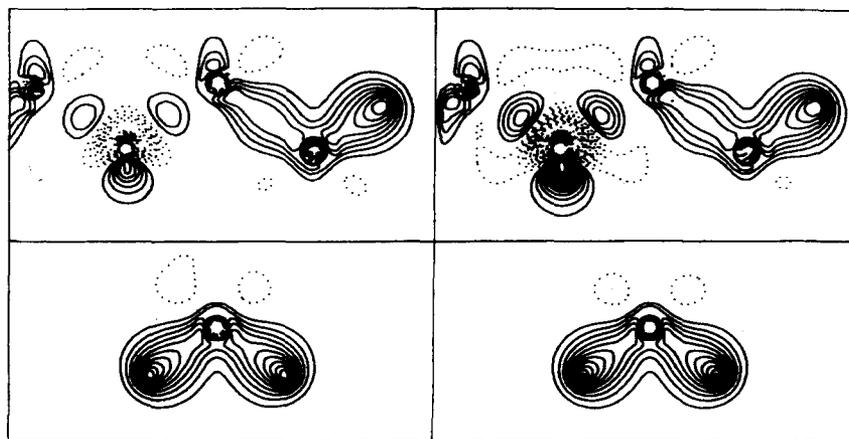

Figure 4. Contour plots of the electron density distribution in 18-crown-6. Subtracted are spherical averaged atomic densities. Left: 18-crown-6; right: construction of CH_3OCH_3 (O) and CH_3CH_2OH (CH_2) stockholder atoms; above: O—C—C plane; below: H—C—H plane. Contour interval: 0.015 a.u., —positive contours, ... negative contours.

tion itself. As stated before, only atoms in similar chemical environments can be compared, so we took for this map the oxygen atom of dimethyl ether, which is bonded to two carbon atoms like in 18-crown-6, and the CH_2 group of ethanol, which is bonded to an oxygen atom and a carbon atom like in 18-crown-6. Especially the resemblance in the CH_2 group is very good. The charge distribution near the oxygen atom however shows more difference, which is reflected in the difference in atomic charge and dipole moment between the oxygen atom in dimethyl ether and 18-crown-6.

The aim of the calculation of stockholder atomic charges and dipole moments is to describe electrostatic interactions. To obtain insight in the electrostatic potential of the stockholder atomic multipoles we draw contour plots of the electrostatic potential of the water molecule in Figure 5. Depicted are the electrostatic potential calculated out of the HFS-DZD wave function and of the stockholder multipoles. We see that beyond the van der Waals radius there is only a minor contribution of the atom quadrupole moments. So the electrostatic potential can be described fairly well by the atomic charges and dipoles. From the stockholder multipoles we calculated the electrostatic potential at the K^+-site (Table V). We see that taking only atomic charges in account gives a very poor result. Atomic dipoles improve the values, and the contribution of quadrupoles is small.

Table V. Electrostatic potential of H_2O at the K^+ site (a.u.)

	free H_2O	$H_2O...K^+$
Atomic charges	−0.011	−0.011
Charges and dipoles	−0.023	−0.029
Charges, dipoles, and quadrupoles	−0.023	−0.030

CONCLUSIONS

The analysis of the charge distribution of $K^+...$18-crown-6 and its fragments shows a good transferability. Contour maps show that the transferability we found for the atomic moments is based on a detailed resemblance of the atomic charge distributions as defined by the stockholder recipe.

In the free molecules the hydrogens play a major role in the charge distribution. They donate electrons to the other parts of the molecules and in that way determine the charges on the other atoms. The hydrogen atoms added to saturate the bonds of the fragments mainly account for the difference between the fragments and 18-crown-6 molecule.

The atomic charges found by the stockholder method are considerably smaller than the ones found by fitting the electrostatic potential[7-10] This means that a good representation of the electrostatic potential by a multipole expansion of
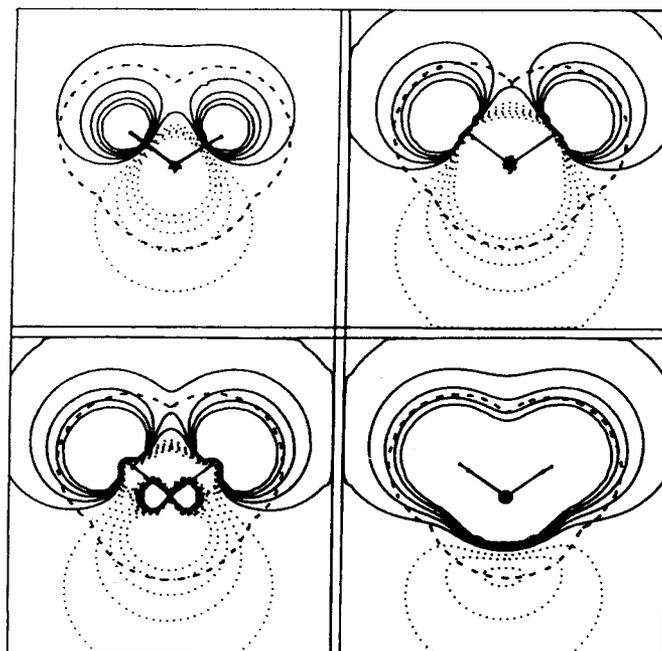

Figure 5. Contour plots of the electrostatic potential of water (a) from stockholder charges, (b) from stockholder charges and dipole moments, (c) from stockholder charges, dipole moments and quadrupole moments, (d) from HFS wave function. Contour interval: .02 a.u. —positive contours, ... negative contours, - - - van-der-Waals radius.

the atomic electron density distribution can only be accurate when this expansion is carried out to a higher order than just the monopole. So the dipole moment component and maybe even higher order moments have to be taken in account. This can be a severe disadvantage of this method, because it gives not a simple expression for the electrostatic potential as is required for simulations of molecular systems by molecular mechanics and molecular dynamics. The merits of the method are that it shows the transferability of the charge distribution different molecules, which can be used to find a simple expression for the electrostatic potential of large molecules.

Effects of polarization by the K^+ cation is to a large extent due to atomic polarization to which the effects of charge transfer between the atoms has to be added. Again the effects are largely transferable.

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