Atomic Charges of the Water Molecule and the Water Dimer

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Atomic charges in the water molecule and the water dimer have been calculated by two different schemes for partitioning the total charge distribution: Mulliken charges and atomic polar tensor-based charges. Large-scale calculations have been carried out where the basis set has been increased systematically toward the basis-set limit. The Mulliken charges are highly sensitive to the choice of basis, and no convergence is observed. In contrast, atomic charges obtained from the trace of the atomic polar tensor exhibit rapid basis-set convergence. We have also investigated the effects of electron correlation on the atomic charges of the water molecule. Finally, the polarization and charge-transfer effects on the atomic charges have been calculated for the water dimer. The importance of such terms in a water potential used in molecular dynamics simulations of aqueous solutions is discussed.

1 Introduction

Properties of condensed phases are governed by the properties of the individual molecules and the intermolecular interactions. The most important contribution to intermolecular forces between polar molecules arises from electrostatic interactions—that is, from the interaction between charge distributions as given by classical electrostatics.[1,2] In intermolecular potentials adopted in molecular dynamics and Monte Carlo simulations of molecules or macromolecules in solution, the molecular charge distribution is usually represented by effective atomic charges. In most cases, these charges are parametrized on the basis of experimental data, obtained from calculations of Mulliken charges or from a fit of the electrostatic potential. In this context, it is important to realize that an atomic charge is not an observable quantity and that no rigorous definition of an atomic charge exists. Rather, the usefulness of the partial atomic charges stems from the fact that their use leads to a rapid convergence of the interaction energy with respect to the order of the expansion in the atomic multipole moments. This is not true for a one-center expansion of the electrostatics, for which the interaction energy does not converge at intermolecular distances shorter than the molecular dimensions. Since for polar systems the electrostatic interactions are dominant, the accuracy and reliability of the atomic charges are of fundamental importance.

The Mulliken approach to the calculation of atomic charges[3] takes as a starting point the observation that the wave function (and thus the charge density) is expanded in basis functions attached to the atomic nuclei. In an atomic basis-set expansion, the charge distribution ρ may be written as

$$\rho = \sum_{kl} D_{kl}\chi_k\chi_l \tag{1}$$

where $\mathbf{D}$ is the density matrix and χ a basis function. The indices k and l run over all basis functions of the system. We may restrict the summation over k to basis functions at nucleus K and the summation over l to basis functions at nucleus L. Integrating over the physical space, a charge q_{KL} assigned to the two nuclei K and L may then be written as

$$q_{\mathrm{KL}} = \sum_{k\in \mathrm{K}}\sum_{l\in \mathrm{L}} D_{kl}S_{kl} = \sum_{k\in \mathrm{K}}\sum_{l\in \mathrm{L}} q_{kl} \tag{2}$$

where $\mathbf{S}$ is the one-electron overlap matrix and q_{kl} a charge assigned to the two basis functions χ_k and χ_l. If $k = l$, q_{kk} is trivially assigned to nucleus K. For the multicenter charges the situation is less clear. Mulliken originally assigned one-half of q_{kl} to nucleus K and the other half to nucleus L, but other schemes have also been proposed.[4−7] Some of these schemes have been generalized to higher-order atomic moments by replacing the overlap matrix in eq 2 with for example the dipole-moment matrix.[4−6,8−10] The reliability of Mulliken charges has been discussed extensively, in particular their dependence on the basis set (see, for example, refs 11, 12).

It should be noted that the electrostatic interaction energies calculated with atomic moments in a Mulliken-type scheme are much less sensitive to the basis set than are the atomic moments themselves.[6] The reason for this behavior appears to be that the atomic moments by definition give the correct molecular moments to the same order as the expansion of the atomic moments and low-order atomic moments seem to give accurate higher-order molecular moments. This has been demonstrated for the water molecule, where the partial charges of the NEMO potential give accurate molecular quadrupole and octopole moments.[13]

For larger molecules, the atomic charges may be derived from fits to the quantum-chemically derived electrostatic potential

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and field around the molecule,[14,15] to the potential and field obtained from a distributed multipole expansion,[16,17] or to the molecular electric moments.[18,19] An alternative approach would be to use distributed moments based on a partitioning of the physical space,[20−23] but these moments appear to give slow convergence toward the true molecular moments.[12]

A different approach has been proposed by Cioslowski,[11,24] and is based on the observation that the dipole moment μ of a system of N fractional charges q_i is given trivially as

$$\mu_\alpha = \sum_{i=1}^{N} q_i r_{i\alpha} \tag{3}$$

where $r_{i\alpha}$ is a Cartesian vector component. If the dipole moment is regarded as a function of r_{ix}, the partial charges may be obtained as

$$q_i = \frac{1}{3} \sum_{\alpha=x,y,z} \frac{\partial \mu_\alpha}{\partial r_{i\alpha}} \tag{4}$$

which is identified as the trace of the *atomic polar tensor* (APT), which contains information also on the vibrational intensities in infrared spectroscopy. It has been noted that the basis-set dependence is modest for these APT charges,[11,25] although a systematic study of their basis-set convergence has not yet been reported.

Although proposed a decade ago, the APT charges have remained largely unexploited.[25−27] One reason may be that they are computationally expensive compared with Mulliken charges, even though they can be rather efficiently calculated using quantum chemical reponse theory[28,29] at the same cost as, for example, nuclear shielding constants. It has also been noted that, for molecules containing double and triple bonds, the APT charges are sensitive to electron correlation.[25] For many molecules, however, the charge distribution itself is sensitive to correlation. For example, in a recent publication, we noted that the inclusion of electron correlation reduces the quadrupole moment of nitroethene by a factor of about two.[30] The representation of the charge distribution (the distributed multipole moments) cannot be expected to behave better than the charge distribution itself, and this behavior appears to be reflected in the correlation dependence of the APT charges.

A large number of water potentials have been used in simulations of liquid water and solvation in aqueous solutions (see, for example, refs 31−33). As a liquid, water has many anomalous properties,[34] being, for example, the only small hydride that remains a liquid at room temperature. All potentials so far presented have problems in modeling all the properties of liquid water at various pressures and temperatures. Since liquid water is a highly polar liquid, the representation of the electrostatics of the water molecule is crucial for an accurate description of the condensed phases.[31] Normally, the electrostatics of water potentials is described by partial charges and sometimes by an additional isotropic one-center polarizability. It is only recently that a more realistic representation of the electrostatics has been adopted in simulations of liquids, using atomic charges, dipole moments, and polarizability tensors.[35]

The aim of the present work is 2-fold. First, we study the basis-set convergence of the Mulliken and APT charges of the water molecule, employing basis sets that may be increased systematically toward the basis-set limit. We also calculate the effects of electron correlation on the APT charges. Next, we investigate how the atomic charges of the water dimer depend on intermolecular distances and the relative orientation, as polarization effects and charge-transfer contributions to the atomic charges may be important for obtaining an accurate potential for modeling liquid water.

TABLE 1: Basis Set Study of the Atomic Charges of the Water Molecule

basis set	q_O^{APT}	q_H^{APT}	q_O^{Mull}	q_H^{Mull}	μ/D
cc-pVDZ	−0.5560	0.2780	−0.3058	0.1529	2.057
cc-pVTZ	−0.5561	0.2781	−0.4828	0.2414	2.025
cc-pVQZ	−0.5619	0.2809	−0.5264	0.2632	2.007
cc-pV5Z	−0.5656	0.2828	−0.5611	0.2806	2.002
cc-pV6Z	n.c.[b]	n.c.[b]	−0.4408	0.2204	1.989
aug-cc-pVDZ	−0.5629	0.2815	−0.2984	0.1492	1.999
aug-cc-pVTZ	−0.5641	0.2821	−0.4387	0.2193	1.983
aug-cc-pVQZ	−0.5639	0.2820	−0.5830	0.2915	1.981
aug-cc-pV5Z	−0.5638	0.2819	−0.8245	0.4122	1.981
daug -cc-pV5Z[a]	n.c.[b]	n.c.[b]	−0.9565	0.4782	1.981
ANO-S[4*s*3*p*2*d*/3*s*2*p*]	−0.5625	0.2813	−0.6714	0.3357	1.991
ANO-S[5*s*4*p*3*d*/4*s*3*p*]	−0.5645	0.2822	−0.9092	0.4546	1.986
ANO-L[4*s*3*p*2*d*/3*s*2*p*]	−0.5573	0.2786	−0.7504	0.3752	1.971
ANO-L[5*s*4*p*3*d*/4*s*3*p*]	−0.5645	0.2823	−0.7837	0.3918	1.980
ANO-L[6*s*5*p*4*d*/5*s*4*p*]	−0.5651	0.2825	−0.6665	0.3332	1.982
ANO-L[4*s*3*p*2*d*1*f*/3*s*2*p*1*d*]	−0.5589	0.2794	−0.6304	0.3152	1.969
ANO-L[5*s*4*p*3*d*2*f*/4*s*3*p*2*d*]	−0.5631	0.2816	−0.8648	0.4324	1.975
ANO-L[6*s*5*p*4*d*3*f*/5*s*4*p*3*d*]	−0.5639	0.2820	−0.8389	0.4184	1.980
ANO-L	−0.5640	0.2820	−0.5757	0.2878	1.982
STO-3G	−0.2109	0.1055	−0.3660	0.1830	1.725
6-31G*	−0.5907	0.2953	−0.8974	0.4487	2.219
6-31G**	−0.5769	0.2885	−0.6810	0.3405	2.182

[a] Each shell of the aug-cc-pV5Z basis set has been extended with one diffuse function according to a geometric series. [b] Not calculated.

2. The Water Molecule

First, we study the water molecule ($r_{OH} = 0.9572$ Å, $\angle_{HOH} = 104.52°$). We have carried out a systematic and extensive basis-set study at the Hartree−Fock (HF) level of the Mulliken and APT charges. We have employed two different families of basis sets: the atomic natural orbital (ANO) basis sets of Widmark and co-workers[36,37] and the correlation-consistent sets of Dunning and co-workers.[38−40] The correlation-consistent basis sets are denoted by cc-pVX Z, where $X \in$ {D,T,Q,5,6}. The corresponding sets augmented with diffuse functions are referred to as aug-cc-pVX Z. We denote the larger primitive ANO basis set[36] by ANO-L and the smaller primitive set[37] by ANO-S. The contraction of the ANO basis sets is given as for example ANO[4*s*3*p*2*d*/3*s*2*p*], where 4*s*3*p*2*d* denotes the contraction of the oxygen basis and 3*s*2*p* the contraction of the hydrogen basis, respectively. Since the ANO and correlation-consistent basis sets may be systematically extended toward the basis-set limit, they are well suited for studying the basis-set convergence of the Mulliken and APT charges. In our calculations, we have used the DALTON program[41] for the atomic polar tensors[29] and the GAUSSIAN program[42] for the Mulliken charges.

From Table 1, we see that, whereas the oxygen APT charge q_O^{APT} is −0.560 ± 0.005 for all ANO and correlation-consistent basis sets, the corresponding Mulliken charge q_O^{Mull} varies between −0.30 and −0.96, with no indication of convergence. Furthermore, augmenting the uncontracted ANO-L basis with diffuse functions in a geometric series, we find that, whereas the Mulliken charges vary by as much as 10% compared with the primitive ANO-L basis, the effect on the APT charges is negligible. Likewise, adding a set of *d*-functions to the hydrogen ANO-L basis and a set of *g*-functions to the oxygen basis (with exponents taken from the cc-pVQZ basis set), we find that the Mulliken charges change by about 30% whereas the APT charges remain unaffected.

For comparison, we have in Table 1 included the STO-3G,[43] 6-31G*,[44] and 6-31G**[44] basis sets, commonly used in studies of intermolecular interactions of large molecules. At the STO-3G level, the APT charges are off by almost a factor of 3 (relative to the basis-set limit) and the dipole moment is in error by 10%. For the APT charges, the 6-31G* and 6-31G** basis sets are rather close to the basis-set limit and we note that the 6-31G** and cc-pVDZ errors are similar. However, the cc-pVDZ dipole moment is much closer to the basis-set limit than is the 6-31G** dipole moment. The Mulliken charges are again more sensitive to the quality of the basis set, and we note that the charges at the 6-31G* and 6-31G** levels differ by as much as 25%.

As noted above, the atomic moments are defined to give the correct molecular moments. The molecular dipole moment, for example, μ_α, is given as

$$\mu_\alpha = \sum_i q_i r_{i\alpha} + \mu_{i\alpha} \tag{5}$$

where $\mu_{i\alpha}$ is the atomic dipole moment. With no atomic dipole moments added, the APT charges give a molecular dipole moment of 1.59 *D*, which is 80% of the quantum-chemically calculated molecular dipole moment. Consequently, the APT dipole moments will give only a small, but not negligible, contribution to the molecular dipole moment. The convergence of the APT moments thus appears to be rapid, whereas the convergence of the Mulliken moments must be highly basis-set dependent. However, since the molecular quadrupole moment is important for describing intermolecular interactions, also the atomic dipole moments, $\mu_{i\alpha}$, must be included in a force field. Atomic dipole moments may be defined analogously to the APT charges.[24]

The effects of electron correlation on the APT charges of water have been calculated using CASSCF[45] and RASSCF[46,47] wave functions. In these wave functions, the orbital spaces are divided into five groups:

(1) *The inactive space.* The inactive orbitals are kept doubly occupied in all configurations. In all calculations, we have included the O1*s* orbital in this space.

(2) *RAS1.* In this study, we allow single and double excitations out of this space.

(3) *RAS2.* All possible occupations of the orbitals are included.

(4) *RAS3.* In this study, we allow single and double excitations into this space.

(5) *Virtual space.* All orbitals are always unoccupied.

The wave functions are denoted by ${}^{inactive}CAS^{RAS2}$ and ${}^{inactive}_{RAS1}RAS^{RAS2}_{RAS3}$, where the subscripts and superscripts give the number of orbitals in each irreducible representation of the C_{2v} point group. In all calculations, we have used the uncontracted ANO-L basis set.

The results are presented in Table 2. The APT charges are reduced by about 10% when electron correlation is included, and most of the correlation effects are accounted for by the standard ${}^{1000}CAS^{4220}$ wave function. Electron correlation is expected to reduce the atomic charges of water since the Hartree−Fock molecular dipole moment is too large and since the atomic charges constitute the most important contribution to the molecular dipole moment. Our results are in reasonable agreement with the QCISD/cc-pVDZ result of −0.492 for the oxygen APT charge.[25]

The effects of electron correlation are about twice as large for the APT charges as for the molecular dipole moment. Since the APT charges give about 80% of the molecular dipole moment at the HF level, correlation effects will have to be as large as 20−30% for the atomic dipole moments, significantly larger than the change of about 10% observed for the APT charges.

TABLE 2: Effects from Electron Correlation to the APT Charges of Water[a]

	q_O^{APT}	q_H^{APT}	μ/D
HF	−0.5639	0.2820	1.980
${}^{1000}CAS^{4220}$	−0.5175	0.2587	1.904
${}^{1000}CAS^{6331}$	−0.5164	0.2582	1.896
${}^{1000}_{2110}RAS^{0000}_{4221}$	−0.5302	0.2651	1.916
${}^{1000}_{0000}RAS^{4220}_{2111}$	−0.5158	0.2579	1.895
${}^{1000}_{0000}RAS^{4220}_{8553}$	−0.5017	0.2509	1.865

[a] The uncontracted ANO-L basis set has been employed.

3. The Water Dimer

As model systems for the interactions in liquid water, two orientations of the water dimer were studied. The first complex is the global minimum of the water dimer with an almost linear hydrogen bond (see inset in Figure 1a). We have here chosen to use a zero-point vibrationally averaged geometry taken from ref 48. The second dimer is a highly symmetric complex with the oxygen atoms close to each other (see inset in Figure 2a). Such non-hydrogen-bonded interactions are present in many structures of ice—although not in normal ice (Ih). It has been suggested that such structures may be the reason that the number of nearest neighbors is larger than four for liquid water, which would otherwise be the ideal number in a tetrahedral arrangement of hydrogen bonds.[49] In a recent study using an empirical potential, this orientation was found to be weakly attractive at an O−O distance of 3.4 Å.[49] In the dimer calculations, we used the ANO-L[6*s*5*p*4*d*3*f*/5*s*4*p*3*d*] set for the APT charges and the uncontracted ANO-L set for the Mulliken charges.

The distance dependence of the atomic charges of the hydrogen-bonded complex is given in Figure 1. The APT charges (Figure 1a,c) and the Mulliken charges (Figure 1b,d) show approximately the same dependence on the O−O distance. As the two molecules approach, the charge distribution in each molecule becomes more polar; the negative oxygen charge becomes more negative and the positive hydrogen charges more positive, the only exception is the charge of H_{dn} (the notation is given in the inset of Figure 1a), which decreases slightly as the distance becomes shorter. This increase in the polarity of the molecules is to be expected since the intermolecular interactions in this way become more attractive as the two molecules approach each other in this orientation.

The water molecule donating a hydrogen to the bond is most strongly affected by the other water molecule. The first peak in the O−O radial distribution functions of liquid water is found at about 3 Å (see, for example, ref 35). At this distance, the charge on O_d is −0.64 and on H_{db} 0.39—that is, the charges of the unperturbed molecule are modified by about 0.09. The effects on O_a are about half as large as for O_d, but, for symmetry reasons, the charge-flow from each hydrogen H_a to O_a is equally large. The changes of the charges on H_a are therefore a factor of 4 smaller than for H_{db}.

We have also calculated the charge flow between the water molecules. The intermolecular charge transfer (CT) effects are much smaller than the intramolecular charge polarization. At 3 Å, the charge flow is −0.01 from the donor to the acceptor, and even at such a short distance as 2.3 Å, the effect is not larger than −0.02.

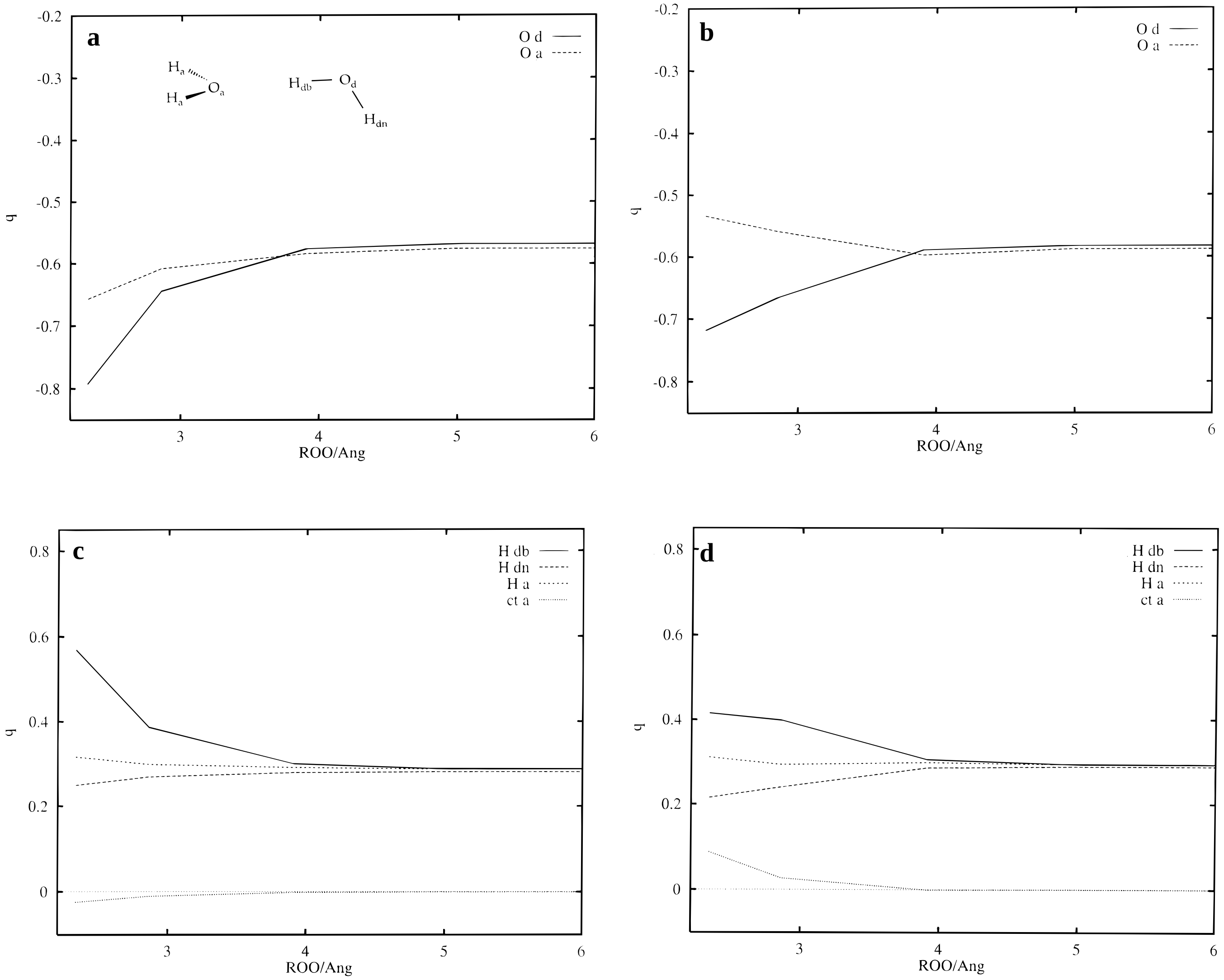

Figure 1. Hydrogen-bonded complex. (a) APT oxygen charges. (b) Mulliken oxygen charges. (c) APT hydrogen charges and charge-transfer effects. (d) Mulliken hydrogen charges and charge-transfer effects.

The Mulliken charges show a behavior similar to that of the APT charges. The differences are mainly in the charge of O_a and in the CT term. The intermolecular charge-transfer flows in the *opposite* direction of that obtained using APT charges and is about four times larger. Charge-transfer terms have previously been discussed for the water dimer, but only in a formulation where the charge-transfer becomes zero for an infinite basis set.[50,51]

The two water molecules in the non-hydrogen bonded complex (see Figure 2) are equivalent, which means that no CT term exists. The charge-polarization terms are smaller than for the hydrogen-bonded complex; at 3.4 Å, we find that q_O^{APT} is −0.54, compared with the unperturbed charge of −0.56. Also for this complex, we find a similar behavior of the APT and Mulliken charges. The charges change in such a manner that the molecules become less polar as they approach each other, which is reasonable since the dipole−dipole interaction is repulsive in this orientation.

4. Discussion

We have studied the atomic charges of the water molecule and how they change when interacting with another water molecule. We have demonstrated that the effects of the surroundings are substantial on the charge distribution of the molecules. These effects will be enhanced in the condensed phase (even if the effects are not additive) as a water molecule may be involved in four hydrogen bonds at the same time.

The main effects of a solvent on the atomic charges may be included by adopting atomic charge polarizabilities[12,52,53]—that is, by taking into account the dependence of the atomic charges on the potential and electric field of the other molecules. Distributed charge and dipole polarizabilities have been difficult to define and to calculate in practice.[12,52,54−57] Distributed polarizabilities have been defined in a topological analysis of the charge density,[53] but charge polarizabilities are defined trivially in the formalism of Cioslowski as higher-order response functions. A major advantage of this approach is that the atomic charges are independent of the representation of the wave function, being defined entirely in terms of the response of the wave function to nuclear displacements.

In simulations of liquids and solutions, polarization effects have mostly been included by dipole polarizabilities (see ref 35, and references therein). Polarization of the charge distribution has also been represented by fluctuating charges.[58−60] However, the charge and dipole polarizabilities give formally two distinct contributions to the induced dipole moment, and they have different distance dependences.[52] Soetens and Millot have recently included both contributions in a simulation of liquid water.[61]

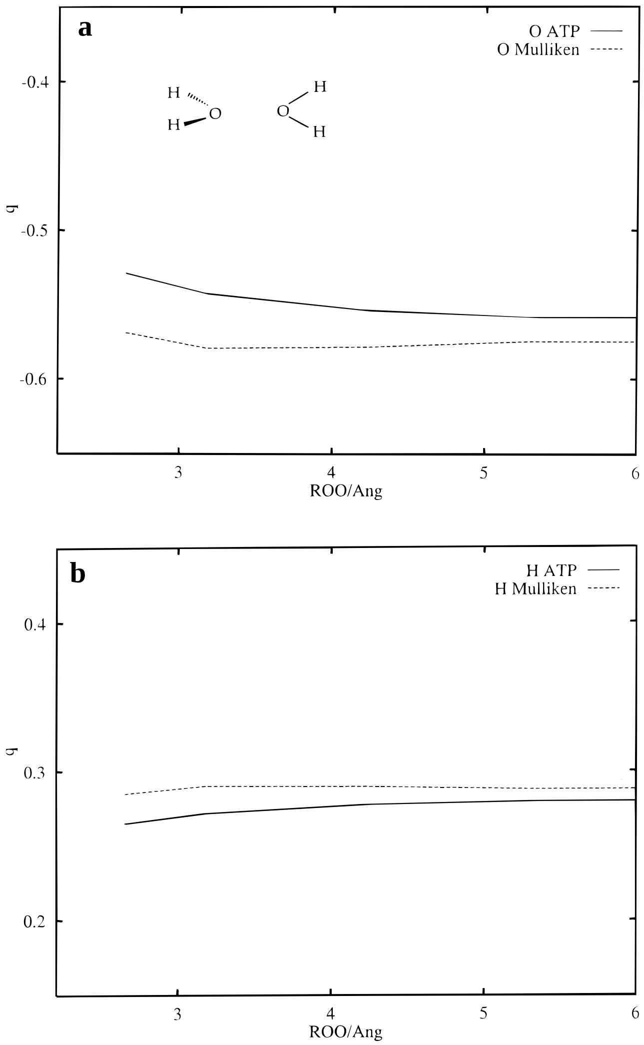

Figure 2. Non-hydrogen-bonded complex. (a) Oxygen charges. (b) Hydrogen charges.

We have investigated the basis-set convergence of the APT charges and the Mulliken charges. Whereas, at the Hartree–Fock level, the APT charges of the water molecule are converged at the augmented DZ level, the Mulliken charges exhibit no such convergence. Even if a generalized Mulliken analysis gives the correct molecular electric moments, the transferability of the atomic charges among molecules must also be rather basis-set dependent. In most potentials used in commercially available programs, the atomic charges are atom-type parameters taken from smaller model systems—for example, in some force fields designed for modeling peptides as AMBER,[62] CHARMM,[63] and GROMOS.[64] Obviously, it would be convenient to calculate such charges with standard quantum chemical methods.

Atom-type charges are often considered to be independent of the conformation of the molecule and of the intermolecular interaction. This approximation gives large errors in the electrostatic potential for small peptides,[65] but a possible approach would be to use native atom-type charges that are perturbed by the electrostatics of the distant parts of the same molecule and the neighboring molecules. Such procedures have been employed, but only to the atomic dipole moments adopting atomic moments and distributed dipole polarizabilities.[66,67] A consistent model for these kinds of intramolecular interactions would be especially suitable for an APT type of response formalism of atomic properties since it does not contain any fitting parameters.

5. Conclusion

We have investigated two different models for calculating atomic charges. For water, the APT charges are converged with respect to the basis set even in a small augmented DZ basis. In contrast, the Mulliken charges show no convergence at all. Our results for the water dimer indicate that charge polarizability terms should be included in a reliable intermolecular potential suitable for simulations of liquid water. The generality and applicability of an APT response formalism for calculating atomic properties to be used in studies of inter- and intramolecular interactions have been discussed.

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