Polarization forces in water deduced from single molecule data

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Intermolecular polarization interactions in water are determined using a minimal atomic multipole model constructed with distributed polarizabilities. Hydrogen bonding and other properties of water-water interactions are reproduced to fine detail by only three multipoles $\mu_H, \mu_O,$ and $\theta_O$ and two polarizabilities $\alpha_O$ and $\alpha_H,$ which characterize a single water molecule and are deduced from single molecule data.

Understanding polarization forces is crucial in many molecular systems such as molecular clusters, liquids, or solids, specifically those containing polar and polarizable molecules. Polarization effects in water are particularly strong, as can be judged by the enhancement of the molecular dipole from 1.855 D for an isolated molecule to 2.6 — 3.2 D in condensed state.\(^1\)\(^2\) Water is a very basic substance.\(^3\) It is a fascinating object to study because of its singular properties, its significance in biological systems, and because it is a classic example of hydrogen bonding.\(^4\) Hydrogen bonding, which itself is one of the most of the force fields use static charges and dipole causes redundancy and leads to unphysical results. This rule is an integral part of the minimal atomic multipole expansion (MAME),\(^5\) which eliminates the redundancies by a careful choice of the minimal set of atomic multipoles based on the Lewis structure of the molecule.

MAME rules lead to the following expression for the electrostatic potential of a single water molecule:

$$
\phi(\mathbf{r}) = \mu_H \frac{(\mathbf{r} - \mathbf{r}_1) \cdot \mathbf{r}_1}{|\mathbf{r} - \mathbf{r}_1|^3} + \mu_H \frac{(\mathbf{r} - \mathbf{r}_2) \cdot \mathbf{r}_2}{|\mathbf{r} - \mathbf{r}_2|^3} + \mu_O \frac{\mathbf{r} \cdot \mathbf{n}}{r^3} + \theta_O \frac{2r^2 - 3(\mathbf{r} \cdot \mathbf{n}_1)^2 - 3(\mathbf{r} \cdot \mathbf{n}_2)^2}{2r^5}.
$$

(1)

Since protons have no charge, neutrality allows no charge on the oxygen either. The dipole $\mu_O$ and quadrupole $\theta_O$ describe the lone pairs on oxygen.\(^5\) Origin is at the oxygen, $\mathbf{r}_{1,2}$ are the positions of protons, $\mathbf{r}_{1,2} = l$, $\mathbf{n} = (\mathbf{r}_1 + \mathbf{r}_2)/|\mathbf{r}_1 + \mathbf{r}_2|$ is the unit vector along the symmetry axis, and $\mathbf{n}_{1,2}$ are unit vectors in the directions of lone pairs (Fig. 1). Experimental geometry has $l = 0.9572$ Å and a nearly tetrahedral bond angle $\beta = 104.52^\circ$ between $\mathbf{r}_1$ and $\mathbf{r}_2.$\(^2\) We take $\mathbf{n}_1$ and $\mathbf{n}_2$ to be at the tetrahedral angle $\beta = 109.47^\circ.$\(^1\) Significant deviation from this value leads to a dramatic deterioration of accuracy of Eq. (1) as seen in the inset.

![Diagram of a single water molecule](image)

**Fig. 1** Geometry of a single water molecule. Vectors $\mathbf{n}_1$ and $\mathbf{n}_2$ point in the direction of the lone pairs on oxygen. The inset shows an effect of varying $\beta$ on the accuracy of (1). $\mu_H, \mu_O$ and $\theta_O$ are re-optimised for every $\beta.$ The vertical bar marks the perfect tetrahedral angle.

It has been recently recognized that hydrogens need not be assigned charges in distributed charge models.\(^5\) The hydrogen’s sole electron participates in the chemical bond and is not centered at the proton. Therefore, hydrogen is best described by an atomic dipole $\mu_H$ placed at the proton and directed along the bond. Assigning both charge and dipole causes redundancy and leads to unphysical results. This rule is an integral part of the minimal atomic multipole expansion (MAME),\(^5\) which eliminates the redundancies by a careful choice of the minimal set of atomic multipoles based on the Lewis structure of the molecule.

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Our goal is to extend the static model to describe the field induced by a polarized molecule subject to external fields. In doing so we again keep only the minimal set of multipoles to avoid redundancies. Charge redistribution part of the molecular polarizability vanishes for water due to the absence of charged sites. Thus we assign polarizabilities to individual nuclei in such a way as to reproduce experimental molecular polarizability. The smallest component is $\alpha_{yy} = 1.4146(3) \text{ Å}^3$ normal to the molecular plane, the next is $\alpha_{zz} = 1.4679(13) \text{ Å}^3$ along the dipole moment, and the largest is $\alpha_{xx} = 1.5284(13) \text{ Å}^3$ in the longest dimension.

Atomic polarizabilities reflect the local atomic environments and need not necessarily be isotropic. Tetrahedral coordination of oxygen suggests to assign it an isotropic polarizability $\alpha_O$. For hydrogens the polarizability $\alpha_H$ along the OH bond may differ from the polarizability $\alpha_\perp$ normal to it. To deduce $\alpha_O$, $\alpha_H$, and $\alpha_\perp$ we express the molecular polarizability,

$$
\begin{align*}
\alpha_{xx} &= \alpha_O + 2\alpha_H \sin^2 \beta/2 + 2\alpha_\perp \cos^2 \beta/2, \\
\alpha_{yy} &= \alpha_O + 2\alpha_\perp, \\
\alpha_{zz} &= \alpha_O + 2\alpha_H \cos^2 \beta/2 + 2\alpha_\perp \sin^2 \beta/2.
\end{align*}
$$

(2)

In a surprise twist, the determinant of this linear system is identically zero. Equations (2) are therefore dependent and possess a solution only if the quantity

$$
\alpha_{xx} \cos^2 \beta/2 + \alpha_{yy}(2 \sin^2 \beta/2 - 1) - \alpha_{zz} \sin^2 \beta/2
$$

is zero. Thus, the model is adequate if the relation holds between the molecular polarizability components. Substituting the experimental values into (3) we get 0.0093Å³, which is indeed close to zero. Two independent equations suggest that one of the atomic polarizabilities can be safely omitted. The natural choice is to set $\alpha_\perp = 0$, implying that the dipole moments on protons can change their value, but not direction. Solving (2) we get

$$
\begin{align*}
\alpha_O &= \alpha_{yy} = 1.4146 \text{ Å}^3, \\
\alpha_H &= (\alpha_{xx} + \alpha_{zz})/2 - \alpha_{yy} = 0.0836 \text{ Å}^3.
\end{align*}
$$

(4)

Thus, the bulk of molecular polarizability comes from the oxygen, which is consistent with its atomic size, while the small polarizabilities on the protons account for the (small) anisotropy of the molecular polarizability tensor.

Three gas-phase multipoles from a density functional calculation, $\mu_H = 0.675 \text{ D}$, $\mu_O = 1.033 \text{ D}$, and $\Theta_O = 1.260 \text{ DÅ}^5$ result in the molecular dipole $\mu = 1.854$ D and the quadrupole components $\Theta = \Theta_{xx} - \Theta_{yy} = 4.973$ DÅ, $\Theta_{zz} = 0.142$ DÅ. These should be compared to experimental data, $\mu = 1.854(6)$ D, $\Theta = 5.126(25)$ DÅ, and $\Theta_{zz} = 0.113(27)$ DÅ.

We again adjust the three atomic multipoles to satisfy the three experimental values precisely to avoid any computational input. The molecular dipole and quadrupole are expressed in terms of the atomic multipoles as

$$
\mu = \mu_O + 2\mu_H \cos \beta/2,
\Theta = 6l\mu_H \sin^2 \beta/2 + 3\Theta_O \sin^2 \beta'/2,
\Theta_{zz} = 2l\mu_H (3 \cos^2 \beta/2 - 1) - \Theta_O (3 \cos^2 \beta'/2 - 1)
$$

(5)

In practice, we face here an almost identical problem, in that the determinant of (5) is small. It becomes zero when an ideal tetrahedral angle is substituted for $\beta$. A relation similar to (3) in this case reads simply $\Theta_{zz} = 0$. Actual $\Theta_{zz}$ is indeed small, but not zero, and $\beta$ deviates noticeably from 109.47°. Nevertheless, smallness of the determinant indicates that the finite accuracy data can be satisfied by a range of atomic multipoles, and so the third equation in (5) cannot be used reliably.

Thus, we use the first two equations to express $\mu_O$ and $\Theta_O$ in terms of $\mu_H$, which guarantees to reproduce experimental $\mu$ and $\Theta$, while keeping reasonable $\Theta_{zz}$. The DFT value $\mu_H = 0.675$ D yields $\mu_O = 1.029$ D and $\Theta_O = 1.352$ DÅ, with $\Theta_{zz} = 0.160$ DÅ. The model is thus completely defined and readily yields the polarization energy $E_P$ for the water dimer, trimer and larger clusters.

Water clusters from dimers on up have been extensively studied with both experiment and theory. Water clusters from dimers on up have been extensively studied with both experiment and theory. Six-dimensional adiabatic energy surface of the dimer has 8 equivalent minima split in a complex fashion by zero-point tunneling motion. Softness of the pair potential requires care when relating it to the experimental observables.

![Fig. 2 Polarization energy (Coulomb + induction), $E_P(\theta_d, \theta_a)$ for water dimer. $R_{OO} = 2.977 \text{ Å}$, and one of the angles is fixed at the minimum value, as the other one is varied. $E_P$ is calculated for the defined system of atomic multipoles and polarizabilities in the standard manner by computing fields of all multipoles of one molecule exerted on the multipoles of another molecule, and solving for self-consistency.](image-url)
acceptor, \( \theta_d \approx 0, \theta_a \approx \beta / 2 = 54.74^\circ \) in our notation. Actual angles deviate slightly from these ideal values and are known with some scatter.

For the experimental geometry we get \( E_P = -7.046 \) kcal/mol. Adding 1.820 kcal/mol for the exchange and dispersion energy [VRT(ASP-W)III\(^8\) value] we get equilibrium binding energy \( D_e = 5.110 \) kcal/mol. The model also yields the total dipole moment of the dimer in excellent agreement with experiment (Table 1).

Since \( E_P \) is only a part of the total interaction, which also contains exchange and dispersion terms, we fix \( R_{OO} \) and analyze the orientation dependence (Fig. 2). The minimum is achieved at \( \theta_d = 2.14^\circ \) and \( \theta_a = 66.26^\circ \), which is close to, but should not be confused with the equilibrium hydrogen-bonded configuration, since other terms may shift the minimum. Rotation of either the donor by \( \Delta \theta_d \approx -\beta \), or the acceptor by \( \Delta \theta_a \approx -\beta \) produces an alternative hydrogen bonded arrangement sketched under the local minima in Fig. 2.

Table 1. Equilibrium binding energy \( D_e \) (kcal/mol) and dipole moment \( \mu_{\text{dim}} \) (Debye) for water dimer. \( \mu_{\text{dim}} \) is the component of \( \mu_{\text{dim}} \) normal to the principal axis. \(^7\)Geometry is fixed at experimental values; \(^7\)projection on the principal axis.

| Method       | \( R_{OO} \) (Å) | \( \theta_d \) | \( \theta_a \) | \( D_e \) | \( \mu_{\text{dim}} \) | \( \mu_{\perp} \) |
|--------------|------------------|----------------|-------------|---------|----------------|----------|
| SAPT-5s      | 2.955            | 6.36°          | 52.83°      | 4.858   |                |          |
| SAPT-5st     | 2.924            | 6.95°          | 58.52°      | 5.026   |                |          |
| VRT(APS-W)III| 2.947            | 1.86°          | 49.27°      | 4.948   | 2.69‡          |          |
| this work\(^1\) | 2.977            | 0.74°          | 59.7°       | 5.110   | 2.67 0.13      | 0.13     |
| Expt.\(^2,27\) | 2.977            | 0.74°          | 59.7°       | 2.67    | 0.38           |          |

In order to further assess the quality of the model, we analyze the energy variation along a path where the exchange and dispersion terms vary little. We choose to rotate the donor by an angle \( \phi \) around the bridging OH bond (Fig. 2). Only a single proton then changes its position and stays far from all the nuclei of the acceptor at all \( \phi \).

Figure 3 shows excellent agreement with all three best pair potentials. Note the small (< 1 kcal/mol) total amplitude of the variation, which is not described by a simple \( \cos \phi \) function. The overall agreement in the full range of \( \phi \) is better than the \( \text{ab-initio-based} \) SAPT-5s\(^9\) potential (the inset). However, at small \( \phi \) we get a near coincidence with the other two curves, VRT(ASP-W)III and SAPT-5st,\(^10\) which are both spectroscopically-tuned. This is not surprising, assuming the spectroscopic tuning is more sensitive to the region near the equilibrium.

Explicit distributed polarizabilities (4) suggest an estimate of the dispersion energy. Due to the fast \( r^{-6} \) decay, the dispersion is dominated by two terms, \( E_{\text{DO}}^0 \propto \alpha_O \alpha_O \) and \( E_{\text{HO}}^0 \propto \alpha_H \alpha_O \). Small \( \alpha_H \) in the second term is compensated by the proximity of the donor hydrogen to the oxygen of the acceptor. Neglecting dispersion nonadditivity and assuming an universal scaling of the dispersion coefficient \( C_6 \approx z \alpha_A \alpha_B \) for \( A \) and \( B \) species, we get \( E_{\text{DO}}^0 = z \alpha_A^2 / R_{\text{DO}} \approx 0.99 \) kcal/mol and \( E_{\text{HO}}^0 = \frac{2}{3} z \alpha_H \alpha_O / (R_{\text{OO}} - l)^6 \approx 0.40 \) kcal/mol for linear hydrogen bond. The total \( E^D = 1.39 \) kcal/mol can be compared to 1.56 kcal/mol from Fig. 3 of Ref. 33. For this crude estimate we used \( z = 344 \) kcal/mol value for Ar. The factor \( \frac{2}{3} \) accounts for the anisotropy of \( \alpha_H \).

\[
E(\phi) = E(0) - E(\phi) \text{ (kcal/mol)}
\]

Fig. 3 Energy variation for water dimer with rotation of the donor around the bridging OH bond.

Since the minimal model is constructed based solely on monomer properties, we may speculate that it should describe larger clusters as well, where the non-pairwise additivity of energy is important.\(^9,29\) Such nonadditivity results from self-consistency of all the induced moments in the cluster,\(^24\) and may be relevant for the cooperativity of hydrogen bonding in protein secondary structures.\(^35\)

This work makes a step towards a chemical model for polarization intermolecular forces by combining minimal atomic multipoles with distributed polarizabilities, which together yield a transparent model for polarization forces in water. Its success raises a question of broader applicability, especially to polarization and hydrogen bonding in peptides and proteins, and in water-protein interactions.

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