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Communication

Charges of TIP4P water model for mixed quantum/classical calculations of OH stretching frequency in liquid water

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ABSTRACT: The potential curves of OH bonds of liquid water are inhomogeneous because of a variety of interactions with other molecules and this leads to a wide distribution of vibrational frequency which hampers our understanding of the structure and dynamics of water molecules. Mixed quantum/classical (QM/CM) calculation methods are powerful theoretical techniques to help us analyze experimental data of various vibrational spectroscopies to study such inhomogeneous systems. In a type of those approaches, the interaction energy between OH bonds and other molecules is approximately represented by the interaction between the charges located at the appropriate interaction sites of water molecules. For this purpose, we re-calculated the values of charges by comparing the approximate interaction energies with quantum chemical interaction energies. We determined a set of charges at the TIP4P charge sites which better represents the quantum mechanical potential curve of OH bonds of liquid water.

The OH stretching frequency of liquid water is sensitive to their surrounding environments and therefore useful information about the molecular structure and dynamics have been obtained from various vibrational spectroscopies probing the OH bonds.[1-8] In those studies, theoretical works play an important role in interpreting experimental data. To exploit the theoretical works, potential energies of OH bonds under various circumstances in liquid water should be calculated by appropriate methods.

Full quantum chemical calculations for the potential energies over a huge number of molecular configurations are very expensive and so a practical choice could be to employ a mixed quantum/classical theory.[9-13] In these methods, based on the assumption of adiabatic separation between the fast OH stretching motion and other slow degrees of freedom, a small subsystem including the stretching motion of a particular OH bond is treated by a full quantum chemical method while its interaction with the remainder of whole system (which is assumed to be frozen by the adiabatic approximation and treated by classical mechanics) is approximately described.[14]

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As an example, the potential energy curve v_0 for an OH stretching coordinate of an isolated water molecule is calculated by a quantum chemical *ab initio* method such as the coupled-cluster theory and the interaction energy curve $v_{\rm int}^{\rm CM}$ between the stretching motion and all other frozen degrees of freedom is approximately calculated by the Coulombic interaction energy between oscillating charges at the charge sites of the water molecule of interest and fixed charges at the charge sites of other water molecules. In that case, an approximate potential energy of an OH stretching motion in liquid water can be constructed by a sum of the two terms: $v = v_0 + v_{\rm int}^{\rm CM}$.

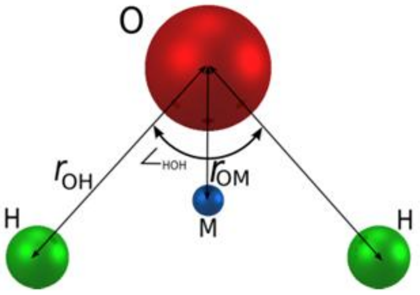

Figure 1. TIP4P water model consists of a Lennard-Jones site at the oxygen atom and three charge sites on two hydrogen atoms and a dummy atom denoted by M. $r_{\rm OH}$ = 0.9572 Å, $r_{\rm OM}$ = 0.15 Å, ∠HOH=104.52°. The charges of TIP4P model are $q_H = 0.52e$ on the hydrogen atoms and $q_{\rm M} = -2q_{\rm H}$ on the dummy atom. In this communication, the value of $q_{\rm H}$ while the sum of the charges is kept zero is re-parameterized for a better description of fluctuating stretching frequency of OH bonds in liquid water.

An acceptable form of $v_{\rm int}^{\rm CM}$ might be the Coulombic interaction energy between the charges of various water models such as SPC, SPC/E,[15] and TIP4P.[16] However, since such models were developed to reproduce a few bulk properties of liquid water, the charges assigned with the models may not show the best performance for the interaction energy of OH stretching motion $v_{\rm int}^{\rm CM}$. In this communication, we determined a better set of charges assigned to the charge sites of TIP4P model (shown in Fig. 1) which is found to be well suited for the potential energy of an OH stretching motion in liquid water. This was done by comparing the Coulombic interaction energy of the charges with the quantum chemical interaction energy calculated by the density functional theory in the level of ωB97X/6-311+G(3df,3pd)[17] using the Gaussian 09 software package.[18] We chose this level of density functional theory since we confirmed[19] that the fundamental frequencies of OH stretching motion in a dimer, trimer, and tetramer of water molecules are predicted by the theory to be very similar to the ones calculated by the coupled-cluster theory[20] including both single and double excitations with perturbative inclusion of triple excitation (CCSD(T))[21] which is often called the gold standard of computational chemistry.

The comparison was made over a number of molecular configurations which were generated from a molecular dynamics (MD) simulation performed under the periodic boundary condition at a time step of 1 fs for 729 TIP4P water molecules at 298 K with a density of 0.997 g/cm3 using GROMACS package.[22] A thousand configurations were collected at every two picoseconds from the MD trajectory that assures their statistical independence. In each configuration, we randomly selected an OH bond of a water molecule and define the position of the hydrogen atom of the bond as the origin of the configuration. The coordinates of other molecules were shifted by the minimum image convention.

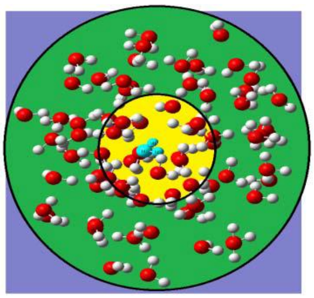

Figure 2. The OH bond of interest is located at the center of box. Other water molecules within the yellow sphere with a radius of 4 Å are fully considered in the quantum chemical calculations. Other water molecules with the green sphere with a radius of 7.831 Å are approximated as point charges and all the others are ignored in the quantum chemical calculations.

We calculated the quantum chemical potential energy as a function of the bond distance for a given configuration of other molecules. The quantum chemical calculations including all of 729 water molecules are not practically possible and therefore only a small subset of the molecules was considered. A cluster of water molecules (about ten molecules) whose oxygen atoms are found to be within a distance of 4 Å from the origin was included in the quantum chemical calculations and other molecules located farther with the distances greater than 4 Å and smaller than 7.831 Å were modeled, in the quantum chemical calculations, as background point charges located at the charge sites of TIP4P model.[16] All other water molecules located farther than 7.831 Å from the origin were ignored in the quantum chemical calculations. The hierarchical level of the model is schematically depicted in Fig. 2.

For a cluster with the background point charges corresponding to the original TIP4P model, keeping all nuclei fixed except those on the molecule at the origin, the relevant OH bond distance was allowed to vary from 0.82 to 1.18 Å with an increment of 0.02 Å while the center of mass and orientation of the molecule were fixed. At the nineteen grid points of the bond distance, we calculated the quantum chemical potential energies and obtained the interaction energies (denoted by $v_{\mathrm{int}}^{\mathrm{QM}}$) for the grid points by subtracting the analogous potential energies of an isolated water molecule from the former. The potential energies of a monomer was calculated by CCSD(T) in the complete basis set limit.[23]

At the grid points, we also calculated the Coulombic interaction energy $v_{\mathrm{int}}^{\mathrm{CM}}$ given by the sum of the pair-wise Coulombic interaction energy over all pairs of point charges in the cluster. For these calculations, all the molecules in the clusters except for the central water were regarded as rigid TIP4P models. The central water molecule was also treated as a TIP4P model but the distance of its OH bond is varied. The charge site at the hydrogen atoms of the central water molecule moves along with the change of atomic positions and the position of its dummy atom is shifted in parallel with the position of its oxygen atom. With those results, we estimated a root mean square of interaction energy difference $\chi \equiv \sqrt{\langle (v_{\mathrm{int}}^{\mathrm{QM}} - v_{\mathrm{int}}^{\mathrm{CM}})^2 \rangle}$ where the bracket denotes an ensemble average over the nineteen grid points as well as over the thousand configurations. With the charges of TIP4P model, we found that χ ($q_{\mathrm{H}} = 0.52$) = 375cm^{-1} as shown in Table 1.

Table 1. Root mean square of interaction energy difference. In all calculations, the charge of dummy atom was kept to be twice of that of hydrogen atom with the opposite sign, $q_{\mathrm{M}} = -2q_{\mathrm{H}}$. The charges giving the minimal χ and the original TIP4P charge are written in bold face.

q_{H} (e)	0.30	0.38	0.39	**0.40**	0.41	0.42	**0.52**
χ(cm^{-1})	228	138	136	**136**	140	147	**375**

Retaining the charge sites, we repeated those calculations of $v_{\mathrm{int}}^{\mathrm{QM}}$ and $v_{\mathrm{int}}^{\mathrm{CM}}$ with different values of charges q_{H} (and $q_{\mathrm{M}} = -2q_{\mathrm{H}}$) and obtained the root mean squares of interaction energy difference for a few values of charges as listed in Table 1. We found that the value of χ becomes minimal when $q_{\mathrm{H}} = 0.4e$ and $q_{\mathrm{M}} = -0.8e$. Those calculations lead us to conclude that the charges of $q_{\mathrm{H}} = 0.4e$ and $q_{\mathrm{M}} = -0.8e$ at the TIP4P charge sites are better suited for the fluctuation of OH stretching frequency in liquid water rather than the charges of the original TIP4P model.

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