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Description of molecule rotation in computer models of water using quaternions

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Abstract. The motion of a rigid molecule in a computer model can be considered as the movement of its center of mass and rotation around an axis passing through this center. This article uses quaternion algebra to describe rotational motion. It provides an opportunity to study rotational motion almost as easily as translational, since the quaternion contains the axis and the angle of rotation in almost explicit form. We use this method to study the rotation of molecules in the molecular dynamics model of water. The distributions of angles between the translational displacement vectors and the axes of rotation of the molecules, as well as between these vectors and the internal vectors of the molecules (dipole moment, normal vector, and HH vector), are investigated. Correlations between the translational and rotational movements of the water molecule are established and the general character of its movement is determined. Appendix contains exact formulas and detailed descriptions of the procedures for using quaternions to describe the rotation of molecules.

Keywords: molecular dynamics simulation, water, translational displacement, angular displacement, correlation of displacement and rotation axis

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The motion of a rigid molecule can be decomposed into the translational displacement of its center, usually the center of mass, and rotation around this center. Translational motion is actively studied both experimentally

and using computer simulation. The study of rotation is completely different. In a real experiment, the rotation of the molecule as a whole is usually not considered. Instead the reorientation of only one of its vectors, for example, the vector of the dipole moment, is studied. Computer simulation gives us the coordinates of each atom of the molecule at any moment of time and, that allows us to describe the rotation of the molecule in more detail. If the changes in the distances between the atoms of the molecule are negligible, the molecule can be considered rigid. In this case, its rotation can be described as the rotation of a solid body in mechanics [1].

The current position of the molecule at time t is represented by a radius vector passing from the Cartesian origin to the center of this molecule. The difference of the radius vectors of the final and initial positions describes the movement of this molecule over a given period of time

$$\mathbf{r}_{2-1} = \mathbf{r}_2 - \mathbf{r}_1. \quad (1)$$

By determining the coordinates of the center of mass and subtracting them from the coordinates of each atom of the molecule, we get the coordinates of these atoms relative to the center of the molecule. Changes in the relative coordinates of atoms in time can be described as the rotation of a molecule around its fixed center. Most often, Euler angles, rotation matrices, or quaternions are used for this [2]. The parameters of the chosen method for describing rotation form a system of coordinate axes of a some specific *orientation space*, which can be used to describe the orientation and rotation of molecules, just as we use the Cartesian coordinate system of the “usual” *position space* to describe the position and displacement of these molecules. The orientation space described with Euler angles has three coordinate axes,

with quaternions four, with rotation matrices nine.

The quaternion algebra turned out to be the most convenient for describing the rotation of molecules of computer models [2-4]. We give the necessary properties of quaternions and calculation procedures in the Appendix. Here we describe only the general ideology of their application for studying the rotational motions of molecules. The main convenience of using quaternions is that they allow the representation of rotation through the most obvious parameters. If the rotation occurs around the \mathbf{u} axis by the angle φ , then the quaternion of this rotation can be written as

$$\mathbf{q} = \cos(\varphi/2) + \mathbf{u} \cdot \sin(\varphi/2). \quad (2)$$

For an unambiguous description of the orientations, it is necessary to indicate the base (origin) orientation of the molecule, which plays the same role as the origin point of the Cartesian coordinate system. The quaternion of rotation \mathbf{q}_1 , which transfers the molecule from this base orientation to the current one, is used as the coordinates of this current orientation in the orientation space. This quaternion \mathbf{q}_1 is an analog of the radius vector \mathbf{r}_1 of the position of the molecule. Comparison of the coordinates of the initial and final orientations of the molecule allows us to determine the quaternion of rotation \mathbf{q}_{2-1} , which transfers the molecule from the initial orientation to the final one – an analog of the translational displacement vector \mathbf{r}_{2-1} . The quaternion of rotational displacement is calculated from the quaternions of initial and final orientation, \mathbf{q}_1 and \mathbf{q}_2 , according to a special formula

$$\mathbf{q}_{2-1} = \mathbf{q}_2 \cdot \mathbf{q}'_1, \quad (3)$$

different from formula (1) for calculating translational displacements. Algorithms for determining the quaternions of the current

orientation and quaternions of rotation are described in Appendix.

The description of a rigid molecule by means of the coordinates of the center of mass and the quaternion of orientation is absolutely complete and unambiguous. Transforming the coordinates of the atoms of the basic configuration according to the quaternion of the orientation of the molecule allows us to obtain the current relative coordinates of its atoms. Adding to them the coordinates of the center of mass of this molecule restores the original molecular dynamic coordinates of its atoms. Thus, instead of 9 coordinates for 3 atoms of a water molecule, it is enough to know 3 coordinates of the center of mass and 4 components of the quaternion. For larger molecules, the savings will be even greater: these 7 parameters will be enough, for example, to replace the 36 coordinates of the atoms of the benzene molecule.

Quaternions were first proposed by William Hamilton in 1843 [5], since then they have been actively studied and have now been described in detail in many mathematical textbooks [6]. They are actively used nowadays to describe rotation in computer games, and there are many publications on the Internet on this topic [7-9]. Quaternions are also used in mechanics [10]. The use of quaternions allowed to create an alternative approach to modeling the dynamics of rigid molecules [3], [11], which, however, is currently used very rarely. Comparison of methods for analyzing rotational mobility using quaternions, Euler angles, and rotation matrices [2] showed that the use of quaternions gives the most stable solutions. Quaternions were also extremely useful in determining the most probable orientations of molecules that are not rigid [12-14]. However, none of the mentioned publications contains a simple

and understandable step-by-step instruction showing how to describe the rotation of rigid molecules in molecular dynamics models using quaternions. We hope that our comments in Appendix can serve as such instructions. They are easily converted to computer programs. The use of these instructions made it very easy to describe the rotation of water molecules when modeling by molecular dynamics. The results of such calculations are presented in sections 3 and 4 of this article.

2. MODELS

We used the molecular dynamics model of water prepared using the LAMMPS molecular dynamics modeling package [15]. The model contains 8000 molecules with the interaction potential TIP4P/2005 [16] in a cubic box with periodic boundary conditions at a pressure of 1 bar and a temperature of 300 K. The simulation step is 2 fs. After preliminary relaxation for 1 ns, a trajectory of 4 ns was calculated, for which instantaneous configurations were recorded every 200 fs. Thus, 20,001 configurations were used for analysis.

The coordinates of the centers of mass and the quaternions of orientations were calculated for each molecule of each recorded configuration. The procedures for calculating orientation quaternions are described in Appendix. The spatial and angular displacements were calculated for time intervals of 0.2, 0.4, 0.6, 1, 2, 4, and 6 ps. For each interval, all possible pairs, separated by such an interval, were used as the initial and final configurations. Thus, for the shortest interval, 20,000 sets of displacements for each of 8,000 molecules were used, and for the longest, 19,970 sets. We believe that trajectory averaging, the duration of which significantly exceeds the lifetime of even the most long-term correlations in models of this size, made

it possible to obtain very reliable averaged well reproducible results.

3. TRANSLATIONAL AND ANGULAR DISPLACEMENTS AND THEIR CORRELATIONS

3.1. CALCULATION OF TRANSLATIONAL AND ANGULAR DISPLACEMENTS

A comparison of the coordinates of the centers of the molecules at the beginning and at the end of each interval was used to calculate the translational displacement vectors according to the formula (1). The directions of these vectors and their lengths were preserved to describe the translational motion. Angular displacements at the same intervals were described using rotational quaternions calculated by the formula (3). According to the formula (2), the rotation angles and directions of the rotation axes were extracted and saved for future use. The procedures for calculating orientations and rotations are described in Appendix. The probability density distributions of translational and angular displacements for different time intervals from 0.2 to 6 ps are shown in **Fig. 1**, translational displacements on the left, angular on the right.

The shapes of all distributions are very similar. A ratio of displacement to duration of time interval is the average velocity in this interval. Therefore, the distributions of translational displacements are well described by the Maxwell distribution (Fig. 1a). In contrast, the distribution of angular displacements noticeably deviates from this shape (Fig. 1b).

The transition between only two orientations is equally described by a rotation by an angle φ around a certain axis and by rotation by an additional angle $2\pi - \varphi$ around a reverse axis of rotation. It is impossible to distinguish them. Therefore, as the angle of rotation, we always took the smaller of these two angles, not exceeding π . For large time intervals, this leads to an overestimation of the distribution and a break at the right edge of the distribution. However, a noticeable number of molecules with such angles was only in the largest interval, and therefore this did not significantly affect the main results.

3.2. ANGLE BETWEEN DISPLACEMENT VECTOR AND AXIS OF ROTATION

In addition to the angle of rotation, the quaternion of rotation explicitly contains

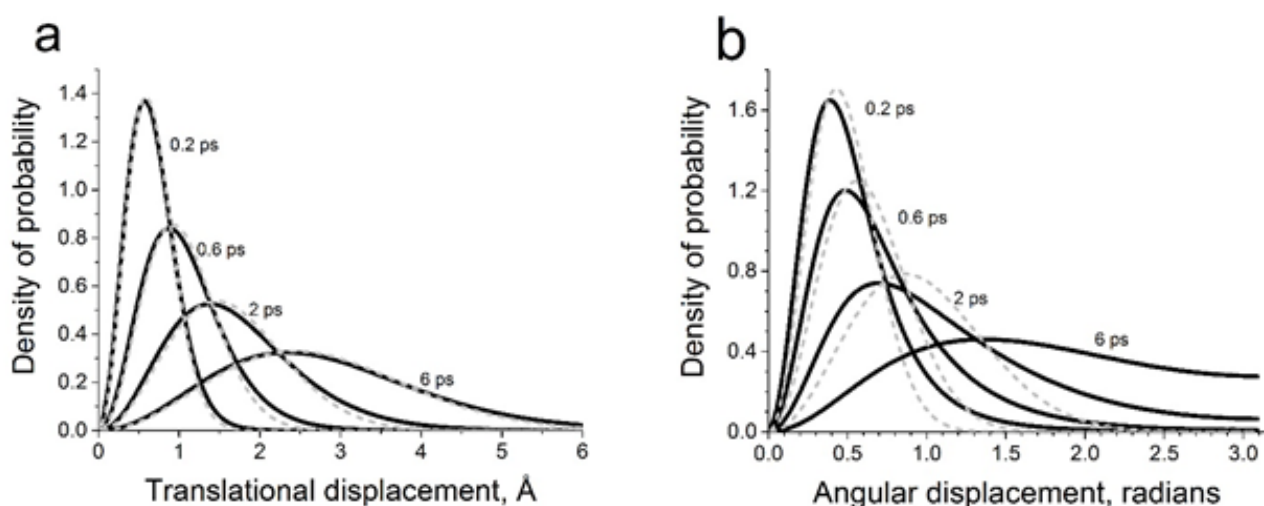


Fig. 1. Distributions of translational (a) and angular (b) displacements of water molecules at $P = 1$ bar, $T = 300$ K for different time intervals (the duration of the intervals is indicated near the curves). Each gray dotted line is the result of approximation by the formula $y = ax^2 \cdot \exp(-bx^2)$.

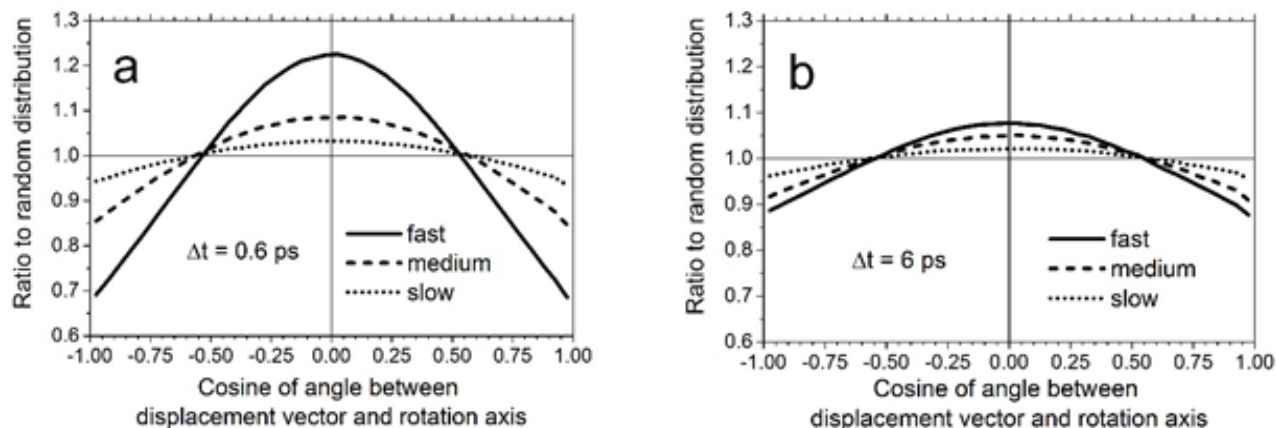


Fig. 2. Distribution of the cosines of the angle between the displacement vectors and the rotation axes. The bold line refers to the fastest molecules, the dotted line to the middle, the dots to the slowest. The groups of the fastest, medium and slowest molecules contained 1/3 of the total number of molecules. Distributions are normalized to random.

the axis of this rotation, which means that we can consider the angles between the axis of rotation and other vectors during the movement of the molecule. **Fig. 2** shows the distribution of the cosines of the angles between the displacement vector and the axis of rotation in the water model. The distribution is normalized to the distribution for randomly oriented vectors, and it shows how often (or less often) this angle was realized in the model compared to the random orientation of the vectors. We divided the molecules according to the magnitude of their translational movement, relating to each group 1/3 of the total number of molecules, and depicted a separate distribution for each group.

Fig. 2a represents the distributions for the interval 0.6 ps, and Fig. 2b for an interval that is 10 times longer. They show that most often the translational displacement vector and the axis of rotation are perpendicular to each other. But the advantage of this orientation is not too large: even for fast molecules, the perpendicular orientation exceeds the random one by 20%, and the parallel one is 30% lower than the random one. Increasing the time interval reduces the deviation from random for all groups.

4. ORIENTATIONS OF INTERNAL VECTORS OF WATER MOLECULES

4.1. ORIENTATION OF THE DIPOLE MOMENT

The quaternion of the current orientation contains all the information about the orientation of the molecule, and therefore contains information about the direction of any of its internal vector. For example, the current direction of the vector of the dipole moment, which we directed along the *X* axis in the base orientation of water, can be obtained by transforming the {1,0,0} vector by the orientation quaternion according to Appendix 6.3. By calculating the angles, firstly, between the direction of the dipole and the displacement vector, and secondly, between it and the axis of rotation, we can find the preferred orientations of the dipole moment relative to the vectors of both of these movements. However, the movement occurs over a certain period of time during which the direction of the dipole can change. We assume that it is most appropriate to use the direction of the internal vector of the molecule in the middle of this interval. Having determined the rotation angle and the axis of rotation over the entire interval, we calculated the median orientation of the molecule by rotating its initial orientation

by half the angle of this rotation around the same axis. **Fig. 3** shows the distribution of the cosines of the angles between the dipole from this mid-orientation with the displacement vector (horizontal) and with the rotation axis (vertical), without dividing the molecules into groups. As it turned out, the most probable is the direction of the dipole moment perpendicular to both the axis of rotation and the displacement vector, and this trend is more pronounced for the dipole moment and the displacement vector. Since the displacement vector and the rotation axis are most often also perpendicular to each other, then obviously all three of these vectors are most often mutually perpendicular.

Note that in addition to the main maximum, there are two noticeable maximums above and below it, for which the dipole moment is still perpendicular to the displacement vector, but it parallel to the axis of rotation. The meaning of these maxima will be considered in the Conclusion.

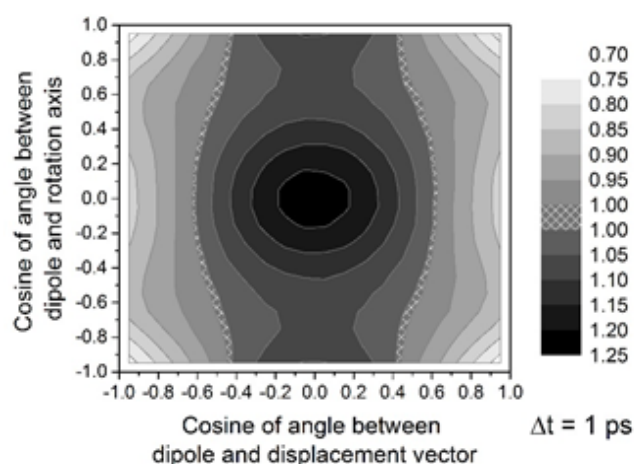


Fig. 3. Two-dimensional distribution of the cosines of the angles between the dipole in the middle orientation and the displacement vector (horizontal) and the same dipole and the axis of rotation (vertical). The distribution is normalized to random: gray shaded stripes are the boundaries separating the areas filled with a probability less than random (light gray) from the areas where the probability is greater than random (dark gray and black).

4.2 ORIENTATION OF THE HH VECTOR

Let's look at the orientation of the HH vector connecting the centers of hydrogen atoms of a water molecule. In the base orientation, it is directed along the Y axis. This vector is perpendicular to the dipole moment and lies with it in the plane of the molecule. Once again, we construct a two-dimensional distribution. This time it is the distribution of the cosines of the angles between the HH vector in the middle orientation in the time interval and the displacement vector of the center of mass of the molecule, as well as between this HH vector and the axis of rotation of the molecule. As follows from **Fig. 4**, the vector HH is most often parallel to the axis of rotation. The distribution is almost independent of the angle between the HH vector and the displacement vector over a given time interval.

4.3. ORIENTATION OF THE NORMAL VECTOR OF A WATER MOLECULE

Fig. 5 shows the distribution of the cosines of the angles between the normal vector to the plane of the water molecule in the middle

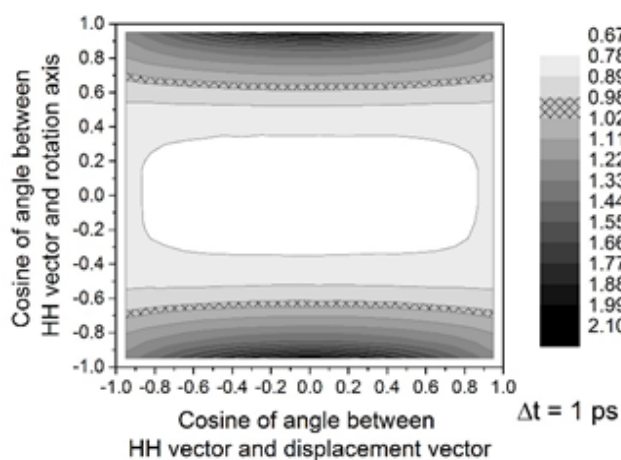


Fig. 4. The two-dimensional distribution of the cosines of the angles between the HH vector in the middle orientation and the displacement vector (horizontal) and this HH vector and the axis of rotation (vertical). Normalization, coloring of more or less probable areas and the boundaries between them are performed in the same way as in Fig. 3.

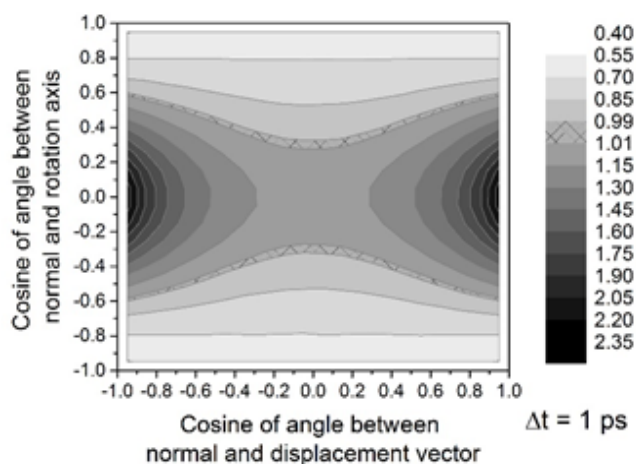


Fig. 5. The two-dimensional distribution of the cosines of the angles between the normal vector to the plane of the water molecule in the middle orientation and the displacement vector (horizontal), and the same normal vector and the rotation axis (vertical). The normalization, coloring of more or less probable areas, as well as the boundaries between them are as in Fig. 3.

orientation and the displacement vector (horizontal) and the same normal vector and the rotation axis (vertical). The normal vector was defined as the perpendicular to the dipole moment and the HH vector, and therefore coincided with the direction of the Z axis in the base orientation. Movements in which the displacement vector is parallel to the normal and the axis of rotation is perpendicular to it are most likely. Moreover, the second orientation is stronger.

5. CONCLUSION

So, we found that:

1. The displacement vector and the axis of rotation are mainly perpendicular to each other.
2. The dipole moment is most often perpendicular to the displacement vector. It is also often perpendicular to the axis of rotation, but there is a noticeable fraction of the molecules for which they are parallel.
3. The HH vector for most molecules is parallel to the axis of rotation, and almost

independent of the orientation of the displacement vector.

4. The displacement vector is often parallel to the normal vector, and the axis of rotation is perpendicular to it, and this second regularity is stronger.

These patterns are observed for any water molecules with any duration of movement. However, they are most pronounced for the fastest molecules in a time interval of about 1 ps.

Fig. 6 shows the proposed scheme of motion of a water molecule, corresponding

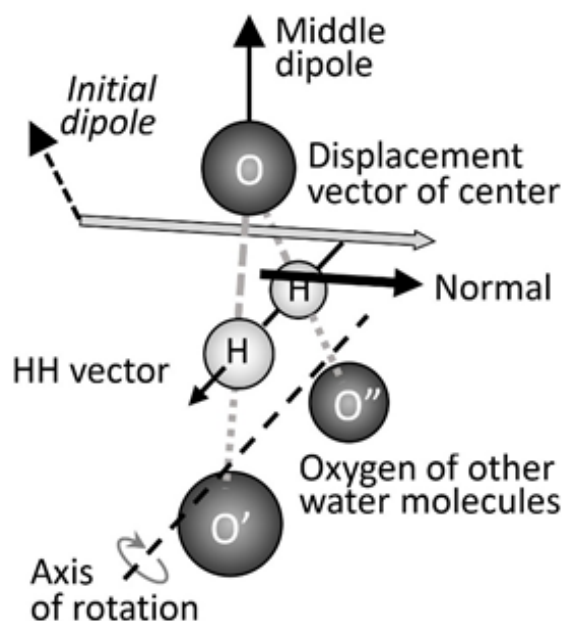


Fig. 6. The proposed scheme of motion of a water molecule, satisfying all the revealed correlations of the angles between the vectors. The water molecule is depicted in the middle orientation of the time interval: O denotes the oxygen atom of this molecule, H show its hydrogen atoms, O' and O'' are the oxygen atoms of nearest molecules to which this molecule have donor hydrogen bonds. The thin up arrow indicates the direction of the vector of dipole moment in the middle orientation, the dashed arrow on the left up corresponds to the dipole at the beginning of the interval. The center of mass displacement vector (gray arrow with a black outline) is parallel to the normal vector (black bold arrow), the HH vector (black arrow passing through the hydrogen centers) is parallel to the rotation axis (dashed line with a circular arrow showing the direction of rotation).

to the detected patterns. Here, the orientation of the water molecule in the middle of the motion interval is schematically shown, as well as the displacement vector, the axis of rotation, and the internal vectors of the molecule; the direction of the dipole in the initial and middle orientations is indicated too. In this scheme, the molecule is "swaying" on two donor hydrogen bonds. Other H-bonds of the molecule are broken or they are noticeably weaker than this pair.

However, all of the above regularities will be observed also if both bonds are acceptor, but then the axis of rotation will be located on the side of the lone electron pair. To elucidate a situation, we construct once again the distribution of angles between the dipole and the displacement vector, as well as with the axis of rotation, similar to Fig. 3, using now a dipole from the initial orientation of the molecule in the interval. This distribution is shown in **Fig. 7**. Location of the main maximum at the angle of 140 degrees between the displacement vector and the initial direction of the dipole

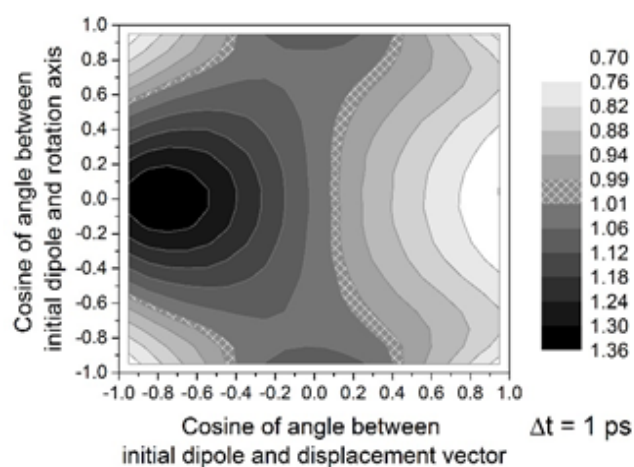


Fig. 7. Two-dimensional distribution of the cosines of the angles between the initial dipole and the displacement vector (horizontal) and the same dipole and the axis of rotation (vertical). Normalization, coloring of more or less probable areas, and the boundaries between them are as in Fig. 3. The main maximum corresponds to angles of 90° between the initial dipole and the axis of rotation and 140° between this dipole and the displacement vector.

moment indicate that most often the strongest bonds on which the water molecule sways are donor ones. If these bonds were acceptor, the angle would be acute.

Fig. 3 contains two additional maxima above and below the main one. These maxima correspond to dipole moments parallel to the axis of rotation. They remained in their former places in Fig. 7, too. We assume that these maxima are formed by molecules in which the pair of the strongest hydrogen bonds consists of one donor and one acceptor. The axis of rotation in this case passes noticeably closer to the center of mass of the molecule from the side of the lone electron than from the hydrogen of the donor bond. If these distances were the same, then the cosines of the angles between the dipole and the axis of rotation for these maxima would be ± 0.7 along each axis. When there are more than two H bonds and they are equally strong, the movement becomes more constrained, the displacements decrease, and the molecule goes beyond the main distribution maxima.

Let's try to determine how far from the center of mass the axis of rotation is located. Suppose that the displacement of the center of mass perpendicular to the axis of rotation occurs exclusively during the rotation of the molecule according to the scheme in Fig. 6. The radius of rotation can be calculated by the formula $R = L/2\sin(\varphi/2)$, where L is the length of the perpendicular displacement to the axis, and φ is the angle of rotation. The radii calculated in this way slowly increase with the movement time. The average radius for time intervals of 0.2 ps, 1 ps, and 2 ps turned out to be 1.28 Å, 1.59 Å, and 1.65 Å, respectively. Even the smallest of these radii shows that the axis of rotation is located far enough from the center of mass of the molecule, almost near the centers of oxygen of the molecules that form hydrogen bonds with this molecule.

The increase in the radius with the increase of the time interval means that the motion of the center of mass of water molecule over long intervals cannot be reduced solely to its rotation. Each molecule simultaneously participates in other movements, including collective movements of different scales. However, the obtained values mainly confirm the scheme shown in Fig. 6.

6. APPENDIX

6.1. BASIC PROPERTIES OF QUATERNIONS

We consider here only those properties of quaternions that are necessary to describe the orientation and rotation of rigid molecules in computer models. Quaternion is a hypercomplex number with one real part and three imaginary with different imaginary units:

$$\mathbf{q} = w + \mathbf{i}x + \mathbf{j}y + \mathbf{k}z \tag{4}$$

where $\mathbf{i}, \mathbf{j}, \mathbf{k}$, are imaginary units. The square of any of them is -1 , and their multiplication by each other is performed similarly to the vector multiplication of unit vectors along the axes of the three-dimensional right Cartesian coordinate system:

$$\begin{aligned} \mathbf{i}\mathbf{i} &= \mathbf{j}\mathbf{j} = \mathbf{k}\mathbf{k} = -1; \\ \mathbf{i}\mathbf{j} &= -\mathbf{j}\mathbf{i} = \mathbf{k}; \\ \mathbf{j}\mathbf{k} &= -\mathbf{k}\mathbf{j} = \mathbf{i}; \\ \mathbf{k}\mathbf{i} &= -\mathbf{i}\mathbf{k} = \mathbf{j}. \end{aligned} \tag{5}$$

A quaternion has four components, and therefore can be represented by a point in four-dimensional space: $\mathbf{q} = \{w, x, y, z\}$. To describe rotation, quaternions must be normalized, therefore: $w^2 + x^2 + y^2 + z^2 = 1$.

A quaternion can also be represented as a pair consisting of a scalar w and \mathbf{v} vector, $\mathbf{q} = w + \mathbf{v}$. The vector \mathbf{v} in this representation consists of the imaginary components of the quaternion, $\mathbf{v} = \{x, y, z\}$. This form of the quaternion describes clearly rotation. So, if a molecule is rotated by an angle φ clockwise around the axis directed along the unit vector

\mathbf{u} , then this rotation is described by the normalized quaternion

$$\mathbf{q} = \cos(\varphi/2) + \mathbf{u} \cdot \sin(\varphi/2) \tag{6}$$

The reverse rotation is described by the complex conjugate quaternion, which is written as

$$\mathbf{q}' = w - \mathbf{i}x - \mathbf{j}y - \mathbf{k}z = \cos(\varphi/2) - \mathbf{u} \cdot \sin(\varphi/2).$$

It describes rotation at the same angle around an axis oriented in the opposite direction.

6.2. PROCEDURE 1. ADDITION OF ROTATIONS

Consider a molecule that has made two rotations one after another. The first rotation is described by the quaternion $\mathbf{q}_1 = \{w_1, x_1, y_1, z_1\}$, the second – by the quaternion $\mathbf{q}_2 = \{w_2, x_2, y_2, z_2\}$. The quaternion of the total rotation is equal to the product of the second quaternion by the first, $\mathbf{q}_{1+2} = \mathbf{q}_2 \cdot \mathbf{q}_1$. Quaternion multiplication is not commutative, you cannot change the order of factors. To calculate the product, let's write the quaternions in the form of sums (4): $\mathbf{q}_{1+2} = (w_2 + \mathbf{i}x_2 + \mathbf{j}y_2 + \mathbf{k}z_2) \cdot (w_1 + \mathbf{i}x_1 + \mathbf{j}y_1 + \mathbf{k}z_1)$. Opening the brackets taking into account the rules of imaginary unit multiplication (5), we obtain the components of the final quaternion \mathbf{q}_{1+2} :

$$\begin{aligned} w_{1+2} &= w_2 \cdot w_1 - x_2 \cdot x_1 - y_2 \cdot y_1 - z_2 \cdot z_1; \\ x_{1+2} &= w_2 \cdot x_1 + x_2 \cdot w_1 + y_2 \cdot z_1 - z_2 \cdot y_1; \\ y_{1+2} &= w_2 \cdot y_1 - x_2 \cdot z_1 + y_2 \cdot w_1 + z_2 \cdot x_1; \\ z_{1+2} &= w_2 \cdot z_1 + x_2 \cdot y_1 - y_2 \cdot x_1 + z_2 \cdot w_1. \end{aligned}$$

An inaccurate representation of the components of the initial quaternions and errors in the numerical calculation may require normalization of the final quaternion.

6.3. PROCEDURE 2. ROTATION OF THE VECTOR

If the vector $\mathbf{v}_0 = \mathbf{i}x_0 + \mathbf{j}y_0 + \mathbf{k}z_0$ turned into the vector $\mathbf{v}_1 = \mathbf{i}x_1 + \mathbf{j}y_1 + \mathbf{k}z_1$ as a result of the rotation described by the quaternion of rotation $\mathbf{q} = w + \mathbf{i}x + \mathbf{j}y + \mathbf{k}z$, then their relation is described by the formula $\mathbf{v}_1 = \mathbf{q} \cdot \mathbf{v}_0 \cdot \mathbf{q}'$. Let's calculate this product in two stages. First, we calculate the auxiliary quaternion $\mathbf{q}_2 = \mathbf{v}_0 \mathbf{q}' = (\mathbf{i}x_0 + \mathbf{j}y_0 + \mathbf{k}z_0) \cdot (w - \mathbf{i}x - \mathbf{j}y - \mathbf{k}z)$. By opening

the brackets and grouping the components of the same type, we get the components of the auxiliary quaternion

$$\begin{aligned} w_2 &= x_0 \cdot x + y_0 \cdot y + z_0 \cdot z \\ x_2 &= x_0 \cdot w - y_0 \cdot z + z_0 \cdot y \\ y_2 &= x_0 \cdot z + y_0 \cdot w - z_0 \cdot x \\ z_2 &= -x_0 \cdot y + y_0 \cdot x + z_0 \cdot w. \end{aligned}$$

The components of the resulting vector $\mathbf{v}_1 = \mathbf{q} \cdot \mathbf{q}_2 = (w + \mathbf{i}x + \mathbf{j}y + \mathbf{k}z) \cdot (w_2 + \mathbf{i}x_2 + \mathbf{j}y_2 + \mathbf{k}z_2)$ are equal

$$\begin{aligned} x_1 &= w \cdot x_2 + x \cdot w_2 + y \cdot z_2 - z \cdot y_2 \\ y_1 &= w \cdot y_2 - x \cdot z_2 + y \cdot w_2 + z \cdot x_2 \\ z_1 &= w \cdot z_2 + x \cdot y_2 - y \cdot x_2 + z \cdot w_2. \end{aligned}$$

The real component of this product is identically equal to zero. An inaccurate representation of the components of the factors and errors in numerical calculations can slightly change the length of the resulting vector. Therefore, it may be necessary to re-normalize this vector.

6.4. PROCEDURE 3. DETERMINING THE QUATERNION OF THE CURRENT ORIENTATION

The current position of the molecule is described by a radius vector drawn from the origin to the point of location of its center of mass. In the same way, we will present the current orientation of the molecule with a quaternion, corresponding to the rotation of the molecule from the base orientation to the current one.

The orientation of a rigid molecule can be described using only two vectors drawn from the center of mass of the molecule to the centers of its two atoms, if these vectors do not belong to the same line. In our works, we determine the basic orientation of any molecule by the same method: the first selected atom (type 1) is located relative to the center of mass in the direction of the X axis, and the second atom (type 2) belongs to the XY plane at positive values of Y . All other atoms are not used to determine the orientation. In a water molecule, we considered oxygen as a type 1 atom, and the first of the hydrogens as

type 2 atom. As a result, the dipole moment of the water molecule in the basic orientation is directed along the X axis, and the line connecting the centers of the hydrogens along the Y axis. The Z axis is the normal to the plane of the molecule.

The components of a quaternion that transfers a molecule from a basic orientation to a current one play the role of the “current coordinates of the molecule in the orientation space”. The basic orientation is described by the zero rotation quaternion $\mathbf{q}_0 = \{1, 0, 0, 0\}$. For any other orientations, such a rotation and the corresponding quaternion must be calculated. It is easier to calculate the quaternion that describes the reverse rotation, and then take the complex conjugate from it.

Let's imagine this reverse rotation as the result of two simple sequential rotations. Suppose that in the current orientation, the direction from the center of the molecule to the center of its type 1 atom is described by a unit-length vector $\mathbf{r}_{10} = \{x_{10}, y_{10}, z_{10}\}$. The first rotation should turn it into a vector $\{1, 0, 0\}$. This can be done by rotating the molecule clockwise around the vector $\mathbf{u}_{10} = \{0, z_{10}, -y_{10}\}$, which is the vector product of the initial and final vectors and, therefore, perpendicular to both of them. The rotation angle is determined by the scalar product of the same vectors, $\varphi_1 = \arccos(x_{10})$. The length of the vector along the rotation axis is $d_1 = \sqrt{z_{10}^2 + y_{10}^2}$. Then the unit vector along this axis is $\mathbf{u}_1 = \{0, z_1, -y_1\}$, where $z_1 = z_{10}/d_1$ and $y_1 = y_{10}/d_1$. Thus, the quaternion of the first rotation is $\mathbf{q}_1 = \{\cos(\varphi_1/2), 0, z_1 \cdot \sin(\varphi_1/2), -y_1 \cdot \sin(\varphi_1/2)\}$.

Let us describe the initial position of the type 2 atom relative to the center of mass with the unit vector $\mathbf{r}_{20} = \{x_{20}, y_{20}, z_{20}\}$. As a result of the first rotation, this vector changes to $\mathbf{r}_2 = \{x_2, y_2, z_2\}$. The projections of this vector can be calculated according to the algorithm

described in procedure 2 (6.3). We will perform the second rotation around the X axis so as not to shift the atom of type 1. As a result, the center of the atom of type 2 should be placed on the XY plane with positive coordinate Y . To do this, we must rotate the molecule through the angle $\varphi_2 = \arccos(y_2 / \sqrt{y_2^2 + z_2^2})$ around the axis $\{1,0,0\}$. Here $\sqrt{y_2^2 + z_2^2}$ is the projection length of the vector \mathbf{r}_2 onto the YZ plane perpendicular to the axis of rotation X , and y_2 is its projection onto the Y -axis. Rotation by this angle will place the vector \mathbf{r}_2 onto the XY plane. Thus, the quaternion of the second rotation should be equal to $\mathbf{q}_2 = \{\cos(\varphi_2/2), \sin(\varphi_2/2), 0, 0\}$. The total quaternion of rotation of this molecule from the current orientation to the basic one is equal to $\mathbf{q}_2 \cdot \mathbf{q}_1$. As the “orientation coordinates” of the molecule, we will use the quaternion of reverse rotation from the basic orientation to the current one; therefore, the quaternion of the current orientation is $\mathbf{q} = (\mathbf{q}_2 \cdot \mathbf{q}_1)' = \mathbf{q}'_1 \cdot \mathbf{q}'_2$.

6.5. PROCEDURE 4. CALCULATION OF THE ANGULAR DISPLACEMENT QUATERNION

We denote the quaternion of the initial orientation of the molecule as $\mathbf{q}_1 = \{w_1, x_1, y_1, z_1\}$, and the quaternion of its final orientation as $\mathbf{q}_2 = \{w_2, x_2, y_2, z_2\}$. The quaternion of rotation, which transfers the molecule from the initial orientation to the final one, is their “difference” $\mathbf{q}_{2,1} = \mathbf{q}_2 \cdot \mathbf{q}_1' = (w_2 + \mathbf{i}x_2 + \mathbf{j}y_2 + \mathbf{k}z_2) \cdot (w_1 - \mathbf{i}x_1 - \mathbf{j}y_1 - \mathbf{k}z_1)$. Opening the brackets and summing the components of one type gives the components of the quaternion of this rotation $\mathbf{q}_{2,1}$.

$$\begin{aligned} w_{2,1} &= w_2 \cdot w_1 + x_2 \cdot x_1 + y_2 \cdot y_1 + z_2 \cdot z_1 \\ x_{2,1} &= -w_2 \cdot x_1 + x_2 \cdot w_1 - y_2 \cdot z_1 + z_2 \cdot y_1 \\ y_{2,1} &= -w_2 \cdot y_1 + x_2 \cdot z_1 + y_2 \cdot w_1 - z_2 \cdot x_1 \\ z_{2,1} &= -w_2 \cdot z_1 - x_2 \cdot y_1 + y_2 \cdot x_1 + z_2 \cdot w_1 \end{aligned}$$

To correct calculation errors, the resulting quaternion should be normalized again.

Note that the rotation between the orientations is equally described by the two

quaternions $\mathbf{q}_{1rot} = \cos(\varphi_{rot}/2) + \mathbf{v}_{rot}$ and $\mathbf{q}_{2rot} = -\cos(\varphi_{rot}/2) - \mathbf{v}_{rot}$. The first describes a rotation through the angle φ_{rot} around the \mathbf{v}_{rot} axis, and the second describes a rotation through the $2\pi - \varphi_{rot}$ angle around the $-\mathbf{v}_{rot}$ axis. Any of them can be obtained as a result of the calculation, and without involving intermediate orientations, we cannot determine which angle is correct. An unambiguous determination of the rotation angle is possible only if it is obviously less than π , when $\cos(\varphi_{rot}/2) \geq 0$. Therefore, if the real component of the rotation quaternion in the calculation turned out to be negative, we reversed the signs of all components of the quaternion.

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