

四元数表示

Quaternion Representation

3次元分子動力学では, 高精度に粒子を動かすため幾つかの方法を使っている。その中でも, 四元数表示は分子動力学の高い運動精度や航空機の運航では必須の方法である。

< Following Sections >

1. Procedures of water molecules by the 5-point method
2. Solving rigid molecules by trans + rotation motions

Ref. Classical Mechanics, H. Goldstein, C. Poole, J. Safko, 3rd Edition, Pearson Education Inc., England, 2003; 「古典力学」, 吉岡書店, 2006.

** Procedures of water molecules by the 5 – points method*
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- a. Five sites are oxygen(O), hydrogen 1 and 2(H), and hydrogen virtual L sites. They have, 0, +0.241e, and – 0.241e charges, respectively. The L1 and L2 are the dummy sites.*
- b. Separate $\mathbf{R}_i$, $\mathbf{V}_i$ and $\mathbf{r}_k$ for water with $i = 1 - N$ molecules, and $\mathbf{s}_{i,k} = (x_{i,k}, y_{i,k}, z_{i,k})$ means for the five sites $k = 1 - 5$.
The separation is done at the starting step only; once determined at $t = 0$, they are constant in time.*
- c. The half time step is first executed for a predictor step, and the full time step is made for advance of time.*
- d. Before the end of one step, the forces are calculated at $\mathbf{r}_{i,k} = \mathbf{R}_i + A^{-1}\mathbf{s}_k$ with the three sites of $k = 1 - 3$, and the L sites are also calculated by algebraic operation.*
- e. After correction of quarternions, go to the beginning of the cycle.
The leap – frog method is used for the plasmas and waters.*

* Each step is translation (1), rotation (2-4), and adding the fields (5-8).

0. Read the quaternions from the file, read (30) e_0, e_1, e_2, e_3 (by Dr. M. Matsumoto, Okayama University).

1. Sum up the five sites and advance $\frac{d\mathbf{V}_i}{dt} = \frac{1}{m_i} \sum_{k=1}^5 \mathbf{F}_{i,k}$, $\frac{d\mathbf{R}_i}{dt} = \mathbf{V}_i$ for each of the translation motion.

2. $\frac{d\mathbf{L}_i}{dt} = \sum_k \left(y_{i,k} F_{i,k}^z - z_{i,k} F_{i,k}^y, \quad z_{i,k} F_{i,k}^x - x_{i,k} F_{i,k}^z, \quad x_{i,k} F_{i,k}^y - y_{i,k} F_{i,k}^x \right)$ for the rotation motion: the sums are made over the five sites.

3. $\omega_{i,\alpha} = (A_{\alpha 1} L_x + A_{\alpha 2} L_y + A_{\alpha 3} L_z) / Im_{i,\alpha}$, the angular frequency for species $A_{\alpha\beta}$ and inertia moments $Im_{i,\alpha}$ at $\alpha = x, y, z$.

4. $\frac{d\mathbf{q}_i}{dt} = \frac{1}{2} Q(e_{i,0}, e_{i,1}, e_{i,2}, e_{i,3}) (\omega_{i,x}, \omega_{i,y}, \omega_{i,z}, 0)$
 $\mathbf{q}_i$ of Q and $\boldsymbol{\omega}$ has four components found in the Goldstein's book.

(continued)

5. Get a new rotation matrix $A_{ij}(e_0, e_1, e_2, e_3)$ written in the book p.205 for the next time step.

6. $\mathbf{r}_{i,k} = \mathbf{R}_i + \begin{pmatrix} A_{11} & A_{21} & A_{31} \\ A_{12} & A_{22} & A_{32} \\ A_{13} & A_{23} & A_{33} \end{pmatrix} \begin{pmatrix} x_{i,k} \\ y_{i,k} \\ z_{i,k} \end{pmatrix}$ at the three sites $\mathbf{r}_{i,k}$ and the position $\mathbf{R}_i$. The dummy sites are determined by algebraic operation.

7. Forces at Coulomb + LJ potentials are calculated using five sites.

8. Normalization (correction) of quaternions is made at every 10 steps, and go to the next time step of Step (1).

Note that a time step is important. It will be $\Delta t = 0.025. - 0.05$, else the code is inaccurate or overflow.

Solving Rigid Molecules by Trans + Rotation Motions

Equations of motion

$$m_{\alpha} \ddot{\mathbf{r}}_{\alpha} = \mathbf{F}_{\alpha} + \sum_{\beta \neq \alpha}^{\ell} \mathbf{F}_{\alpha\beta}$$

$\alpha, \beta = 1, \dots, \ell$ (atoms in the molecule)

Motion of translation

$$M_i \ddot{\mathbf{R}}_i = \sum_{\alpha=1}^{\ell} \mathbf{F}_{\alpha}$$

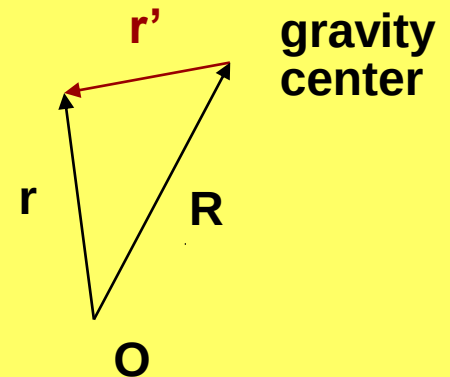
$$\mathbf{R}_i = \frac{\sum_{\alpha=1}^{\ell} m_{\alpha} \mathbf{r}_{\alpha}}{\sum_{\alpha=1}^{\ell} m_{\alpha}}$$

$$M_i = \sum_{\alpha=1}^{\ell} m_{\alpha}$$

Rigid body rotation

Make vector product with $\mathbf{r}'$ from the left side

$$\frac{d}{dt} \left(\sum_{\alpha=1}^{\ell} \mathbf{r}'_{\alpha} \times m_{\alpha} \dot{\mathbf{r}}'_{\alpha} \right) = \sum_{\alpha=1}^{\ell} \mathbf{r}'_{\alpha} \times \mathbf{F}_{\alpha}$$



$$\frac{d\mathbf{L}_i}{dt} = \mathbf{N}_i$$

$$\mathbf{L}_i = \sum_{\alpha=1}^{\ell} \mathbf{r}'_{\alpha} \times \mathbf{p}'_{\alpha}$$

total angular momentum

$$\mathbf{N}_i = \sum_{\alpha=1}^{\ell} \mathbf{r}'_{\alpha} \times \mathbf{F}_{\alpha}$$

sum of torque

Solving Rigid Molecules (2)

Velocity of each atom on the rotating frame

$$\frac{d\mathbf{r}'_\alpha}{dt} = \boldsymbol{\omega} \times \mathbf{r}'_\alpha$$

$$\begin{aligned} \mathbf{L}_i &= \sum_{\alpha} \mathbf{r}'_\alpha \times m_{\alpha} \dot{\mathbf{r}}'_\alpha \\ &= \sum_{\alpha} m_{\alpha} \mathbf{r}'_\alpha \times (\boldsymbol{\omega} \times \mathbf{r}'_\alpha) \\ &= \sum_{\alpha} m_{\alpha} \{ \mathbf{r}'_\alpha{}^2 \boldsymbol{\omega} - (\boldsymbol{\omega} \cdot \mathbf{r}'_\alpha) \mathbf{r}'_\alpha \} \end{aligned}$$

Total angular momentum of the rigid body is written

$$\mathbf{L} = \mathbf{I} \boldsymbol{\omega}$$

inertial moment

$$\mathbf{I} = \begin{pmatrix} \sum_{\alpha} m_{\alpha} (y_{\alpha}'^2 + z_{\alpha}'^2) & - \sum_{\alpha} m_{\alpha} x_{\alpha}' y_{\alpha}' & - \sum_{\alpha} m_{\alpha} x_{\alpha}' z_{\alpha}' \\ - \sum_{\alpha} m_{\alpha} y_{\alpha}' x_{\alpha}' & \sum_{\alpha} m_{\alpha} (z_{\alpha}'^2 + x_{\alpha}'^2) & - \sum_{\alpha} m_{\alpha} y_{\alpha}' z_{\alpha}' \\ - \sum_{\alpha} m_{\alpha} z_{\alpha}' x_{\alpha}' & - \sum_{\alpha} m_{\alpha} z_{\alpha}' y_{\alpha}' & \sum_{\alpha} m_{\alpha} (x_{\alpha}'^2 + y_{\alpha}'^2) \end{pmatrix}$$

Euler Equation for Rigid-Body Rotation

Derivative d'/dt viewed on the rotating frame

$$\frac{d\mathbf{L}_i}{dt} = \frac{d'\mathbf{L}_i}{dt} + \boldsymbol{\omega}_i \times \mathbf{L}_i = \mathbf{N}_i \quad \text{Euler equation}$$

$$\frac{d'L_x}{dt} + (\omega_y L_z - \omega_z L_y) = N_x$$

$$\frac{d'L_y}{dt} + (\omega_z L_x - \omega_x L_z) = N_y$$

$$\frac{d'L_z}{dt} + (\omega_x L_y - \omega_y L_x) = N_z$$

By choosing a proper molecule frame (principal coordinate),
the matrix becomes a constant of motion

$$L_x = I_x \omega_x$$

$$L_y = I_y \omega_y$$

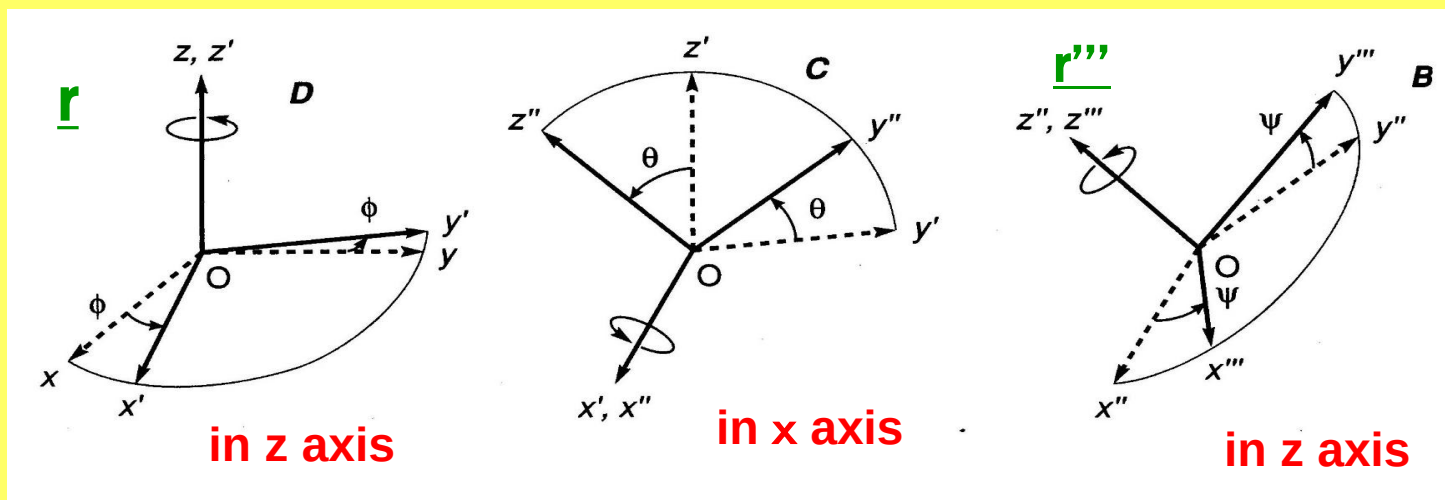
$$L_z = I_z \omega_z$$

$$I_x \dot{\omega}_x - (I_y - I_z) \omega_y \omega_z = N_x$$

$$I_y \dot{\omega}_y - (I_z - I_x) \omega_z \omega_x = N_y$$

$$I_z \dot{\omega}_z - (I_x - I_y) \omega_x \omega_y = N_z$$

Euler Angle Representation



Molecular
frame “”

$$\begin{aligned} \mathbf{r}''' &= \mathbf{BCD}\mathbf{r} \\ &= \mathbf{A}\mathbf{r} \end{aligned}$$

Hereafter, $\mathbf{r}'$ is
simply written $\mathbf{r}$

Rotation matrix is unitary

$$\mathbf{A}^t = \mathbf{A}^{-1}$$

Rotation matrix

$$\mathbf{A} = \mathbf{BCD}$$

$\mathbf{A}(\phi, \psi, \theta)$ representation

$$= \begin{pmatrix} \cos \phi \cos \theta - \sin \phi \sin \theta & \cos \phi \sin \theta + \sin \phi \cos \theta & \sin \phi \sin \theta \\ -\sin \phi \cos \theta - \cos \phi \sin \theta & -\sin \phi \sin \theta + \cos \phi \cos \theta & \cos \phi \sin \theta \\ \sin \theta \sin \phi & -\sin \theta \cos \phi & \cos \theta \end{pmatrix}$$

Euler Angle Representation

$$\mathbf{r} = \mathbf{R} + \mathbf{A}^t \mathbf{r}'''$$

$$\omega_\phi = \dot{\phi}, \quad \omega_\theta = \dot{\theta}, \quad \omega_\psi = \dot{\psi}$$

Time derivatives of
Euler angles

$$\boldsymbol{\omega} = \mathbf{BC} \begin{pmatrix} 0 \\ 0 \\ \dot{\phi} \end{pmatrix} + \mathbf{B} \begin{pmatrix} \dot{\theta} \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ \dot{\psi} \end{pmatrix}$$

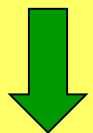
Molecular frame

$$\dot{\phi} = \frac{\omega_x \sin \phi + \omega_y \cos \phi}{\sin \theta}$$

$$\dot{\theta} = \omega_x \cos \phi - \omega_y \sin \phi$$

$$\dot{\psi} = \omega_z - \frac{(\omega_x \sin \phi + \omega_y \cos \phi) \cos \theta}{\sin \theta}$$

Singular at $\theta = 0$, or π !!



To be safe from singularity, the quaternions method is used to connect with the molecular frame.

Use Quaternion in Place of Angles

$$e_0 = \cos \frac{\theta}{2} \cos \frac{\phi + \psi}{2}$$

$$e_1 = \sin \frac{\theta}{2} \cos \frac{\phi - \psi}{2}$$

$$e_2 = \sin \frac{\theta}{2} \sin \frac{\phi - \psi}{2}$$

$$e_3 = \cos \frac{\theta}{2} \sin \frac{\phi + \psi}{2}$$

Classical Mechanics (3rd Edition)
H. Goldstein , C.P. Poole, J.Safko,
Pearson Education Inc., England 2003.

Only three of them are independent
to avoid a gimbal lock

Quaternion representation (4.47')

Rotation matrix

$$\mathbf{r} = \mathbf{R} + \mathbf{A}^t \mathbf{r}'''$$

$$\mathbf{A} = \begin{pmatrix} e_0^2 + e_1^2 - e_2^2 - e_3^2 & 2(e_1 e_2 + e_0 e_3) & 2(e_1 e_3 - e_0 e_2) \\ 2(e_1 e_2 - e_0 e_3) & e_0^2 - e_1^2 + e_2^2 - e_3^2 & 2(e_2 e_3 + e_0 e_1) \\ 2(e_1 e_3 + e_0 e_2) & 2(e_2 e_3 - e_0 e_1) & e_0^2 - e_1^2 - e_2^2 + e_3^2 \end{pmatrix}$$

Time derivative of
quaternions
 e_0, e_1, e_2, e_3

$$\begin{pmatrix} \dot{e}_0 \\ \dot{e}_1 \\ \dot{e}_2 \\ \dot{e}_3 \end{pmatrix} = \frac{1}{2} \begin{pmatrix} -e_1 & -e_2 & -e_3 & e_0 \\ e_0 & -e_3 & e_2 & e_1 \\ e_3 & e_0 & -e_1 & e_2 \\ -e_2 & +e_1 & e_0 & e_3 \end{pmatrix} \begin{pmatrix} \omega_{x'} \\ \omega_{y'} \\ \omega_{z'} \\ 0 \end{pmatrix}$$

Results of Angles and Quaternions

$$(e1^2 + e2^2)/(\sin \theta)^2 = \cos^2 + \sin^2 = 1$$

$$(e0^2 + e3^2)/(\cos \theta)^2 = 1$$

$$\therefore |\sin \theta| = \sqrt{e1^2 + e2^2}$$

$$e2/e1 = \tan (\phi - \psi)/2$$

$$e3/e0 = \tan (\phi + \psi)/2$$

$$\rightarrow \arctan (e2/e1) = (\phi - \psi)/2$$

$$\arctan (e3/e0) = (\phi + \psi)/2$$

$$\therefore \phi = \arctan (e3/e0) + \arctan (e2/e1)$$

$$\psi = \arctan (e3/e0) - \arctan (e2/e1)$$