Replace the Molecule in Clusters

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To use the QVP1 method, the essential step is to replace the molecule you study in the trajectory with the isolated one, or say, to replace it with the un-perturbed one. Considering the fact that motions you do not directly study, even when the motion is an intramolecular one, should be considered as the 'environment', this kind of replacement is not that straight forward.

To replace the in-cluster molecule with the isolated one, we need the following steps.

1. Translation;

2. Rotation;

3. Project the IR-active vibration out;

4. Add the vibrating coordinates back.

Let us define the symbols first. Cartesian coordinates of the atoms in the isolated N-atom molecule are denoted by $\mathbf{R}$ and the equilibrium geometry $\mathbf{R}^{\mathrm{e}}$. The ith normal mode coordinate is written as Q_i and we have

$$\mathbf{R} = \mathbf{R}^{\mathrm{e}} + \sum_i Q_i \cdot \boldsymbol{\xi}_i, \tag{1}$$

where $\boldsymbol{\xi}_i$ stands for the ith normal mode's vector. For in-cluster molecule, $\mathbf{R}'$ is used to denote Cartesian coordinates. x_i, y_i, z_i and x_i', y_i', z_i' are used to describe the Cartesian coordinate in three orthogonal orientations of the ith atom. Note that the $\mathbf{R}$ and its friends are all vectors, or said one column matrices.

First, we perform the translation. Just calculate the centre of mass for the in-cluster molecule

$$w'_{\mathrm{COM}} = \frac{\sum_i m_i w'_i}{\sum_i m_i} \quad (w = x, y, z). \tag{2}$$

and the translation $\mathbf{t}$ can be easily defined as

$$\mathbf{t} = (\underbrace{x'_{\mathrm{COM}}, y'_{\mathrm{COM}}, z'_{\mathrm{COM}}, x'_{\mathrm{COM}}, y'_{\mathrm{COM}}, z'_{\mathrm{COM}}, \ldots, x'_{\mathrm{COM}}, y'_{\mathrm{COM}}, z'_{\mathrm{COM}}, \ldots, x'_{\mathrm{COM}}, y'_{\mathrm{COM}}, z'_{\mathrm{COM}}}_{3N})^{\mathsf{T}}. \tag{3}$$

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Then, rotation. Here, we will follow Damm *et al.*'s algorithm in *BioPhys. J.*, **90**, 4558-4573 (2006). In this particular project, since the molecule can be thought as a rigid body, we use the standard RMSD (sRMSD) fitting. The main idea is introduced as follow.

Consider we have two molecular structures with a little bit deformation, say X and Y, in Cartesian coordinates, with their centres of mass as the origins. For convenience, X and Y are $N \times 3$ matrices. Note that in this document, $N \times M$ means that the matrix has N rows and M columns. In FORTRAN, we write such matrix as

```
REAL*8::X(N,M)
```

for example. Therefore, the covariance matrix R is written

$$R = Y^{\mathsf{T}}\mathrm{diag}(\mathbf{m})X \tag{4}$$

and it is a 3×3 matrix, where $\mathbf{m}$ is vector formed by atomic masses. Further, you get the square of R, R^2

$$R^2 = R^{\mathsf{T}}R. \tag{5}$$

R^2 is then a real symmetry matrix. Diagonalize it, you get the eigenvectors, which form a 3×3 matrix A', and eigenvalue $\lambda_i(i = 1, 2, 3)$. Sort the eigenvectors with their corresponding eigenvalues decreasing. Let us call the matrix formed by the sorted eigenvectors A. Generally, vectors in A should obey $A_3 = A_1 \times A_2$ to deal with plane molecules. Then we calculate

$$B' = RA. \tag{6}$$

Normalize B' to get B. Generally, vectors in B should obey $B_3 = B_1 \times B_2$. The rotation matrix is then

$$\hat{U}_{\mathrm{rot}} = BA^{\mathsf{T}}, \tag{7}$$

noting that the formulas in Kabsch's and Damm *et al.*'s papers are all WRONG (here I use large font and red colour to express my anger), which can operate on X^{T}

$$X'^{\mathsf{T}} = \hat{U}_{\mathrm{rot}}X^{\mathsf{T}} \tag{8}$$

to minimize sRMSD of the two structures, which reads

$$\mathrm{sRMSD} = \left(\frac{1}{N}\sum_i d_i^2\right)^{1/2}, \tag{9}$$

where

$$d_i = [(Y_{ix} - X'_{ix})^2 + (Y_{iy} - X'_{iy})^2 + (Y_{iz} - X'_{iz})^2]^{1/2}. \tag{10}$$

That is all for rotation.

Notice again that the rotation operator is a 3×3 matrix. It is easy to write it as a $3N \times 3N$ matrix. However, in order to consist with the literature and for the elegance of mathematics, we perform all the rotation in X and Y and the vibration in $\mathbf{R}$ and its 'prime versions'.

In this document, for elegance, I will omit all the $X \longleftrightarrow \mathbf{R}$ conversion. In FORTRAN, use the following codes to complete this

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X=TRANSPOSE(RESHAPE(R,(/3,N/)))
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and

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R=RESHAPE(TRANSPOSE(X),(/3*N/))
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To project the studying motion $\boldsymbol{\xi}_k$ out, the in-cluster molecule is first moved to the isolated molecule's place and then perform the projection. We have

$$\mathbf{R}'' = \hat{U}_{\text{rot}}^{\mathsf{T}}(\mathbf{R}' - \mathbf{t}). \tag{11}$$

Also, we have the displacement coordinate

$$\Delta\mathbf{R}'' = \mathbf{R}'' - \mathbf{R}^{\text{e}}, \tag{12}$$

and the so-called mass-weighted version of displacement coordinate $\Delta\tilde{\mathbf{R}}''$ got from multiply $\sqrt{m_i}$ to the ith atom's displacement. Then project the motion studied $\boldsymbol{\xi}_k$ out,

$$\Delta'\tilde{\mathbf{R}}'' = \Delta\tilde{\mathbf{R}}'' - \tilde{\boldsymbol{\xi}}_k^{\mathsf{T}}\Delta\tilde{\mathbf{R}}'' \cdot \tilde{\boldsymbol{\xi}}_k \tag{13}$$

to make sure the 'environment' motions remains untouched and the motion we want to use QVP1 to deal with fix to Q_k^{e}. Note that all symbols with a tilde mean the mass-weighted ones. After that we have to add the motion back (in quantum mechanics picture, or in this case, PODVR grids). We have the jth PODVR grid

$$\mathbf{R}_j''' = \mathbf{R}^{\text{e}} + \Delta'\mathbf{R}'' + r_j \cdot \boldsymbol{\xi}_k. \tag{14}$$

The final in-cluster coordinate then be

$$\mathbf{R}_j'''' = \hat{U}_{\text{rot}}\mathbf{R}_j''' + \mathbf{t}. \tag{15}$$

Some comments should be made to the method presented here. Readers may have noticed that all steps described here are reversible. Therefore, this method honestly represents the molecule's shape and position in clusters. The reason why we do not use vibration modes directly is that the linear normal mode is not a good way to represent the rotation, which may lead to numerical error. Rotation part in this project is very important because you can see in Eq. (14), the reference point used is actually $\mathbf{R}^{\text{e}} + \Delta'\mathbf{R}''$. If rotational normal modes is mixed in $\Delta'\mathbf{R}''$, then the whole method would be skewed because $\boldsymbol{\xi}_k$ is wrong.