数理解析研究所講究録
第1692巻 2010年 46-56

Dynamical Mechanisms for Collective Motions of Nanostructures*

Tomohiro Yanao †

Department of Applied Mechanics and Aerospace Engineering
Waseda University, Tokyo 169-8555, Japan

Abstract

We present dynamical mechanisms for conformational transitions of atomic clusters. A method called hyperspherical mode analysis is introduced, which makes it possible to analyze energy transfer between intramolecular vibrational modes. By using this method, we identify a small number of reactive modes that essentially dominate conformational transitions of atomic clusters by acquiring a large amount of energy. We also identify "trigger modes" that inject energy into the reactive modes through the mode coupling to initiate the conformational transitions. The trigger mechanisms for conformational transitions presented here should be widely applicable to molecular reactions in which a system changes its overall mass distribution in a significant way. [Joint work with Wang Sang Koon (Caltech) and Jerrold E. Marsden (Caltech).]

1 Introduction

Conformational transitions of complex molecular systems, such as nanoclusters and biopolymers, are typically collective motions that involve a large number of degrees of freedom in a highly coherent manner. It has been a significant challenge to understand the general mechanisms for such collective motions. The purpose of the report is to shed light on the mechanisms for collective motions of complex molecular systems by using a novel method of mode analysis.

The mode analysis introduced here is based on the framework of geometric mechanics and the associated gauge theory for the n-body systems with rotational symmetry, which have been developed for decades by Marsden [1–3], Kummer [4], Guichardet [5], Iwai [6, 7], Tachibana [8], Littlejohn [9–12], and their coworkers. It is also based on the framework of hyperspherical coordinates developed by Eckart [13], Chapuisat [14, 15],

*This report is based on the results presented in the joint paper [T. Yanao, W. S. Koon, and J. E. Marsden, J. Chem. Phys. **130**, 144111 (2009)].

†E-mail: yanao@waseda.jp

Kuppermann [16–18], Aquilanti [19–22], and their coworkers. By merging the frameworks of geometric mechanics and the hyperspherical coordinates, we have developed a method called hyperspherical mode analysis for the study of the dynamics of complex molecular systems.

In this report, we summarize the framework of the hyperspherical mode analysis and apply it to the conformational transition dynamics of a six-atom Morse cluster called M_6. This cluster serves as an illustrative model for conformational transitions of molecular systems. We construct a reaction coordinate for the conformational transitions of the atomic cluster. We then identify "trigger modes" that inject energy into the reactive modes through the mode coupling to initiate the conformational transitions. Finally, we discuss the possibility of controlling conformational transitions of molecular systems based on the trigger mechanisms presented here.

2 Expression for kinetic energy of an n-atom system

In this section, we summarize the expression for kinetic energy of an n-atom system in the hyperspherical coordinates. This expression serves as a basis for the hyperspherical mode analysis. Given a system of n atoms, with masses m_i $(i = 1, \cdots, n)$ and positions $\boldsymbol{r}_i = (r_{ix}, r_{iy}, r_{iz})^T$, its overall translational degrees of freedom can be eliminated via the introduction of the $(n-1)$ mass-weighted Jacobi vectors

$$\boldsymbol{\rho}_i = \sqrt{\mu_i}\left(\frac{\sum_{k=1}^{i} m_k \boldsymbol{r}_k}{\sum_{k=1}^{i} m_k} - \boldsymbol{r}_{i+1}\right) \qquad (i = 1, \cdots, n-1), \tag{1}$$

where μ_i are the reduced masses,

$$\mu_i = \frac{m_{i+1}\sum_{k=1}^{i} m_k}{\sum_{k=1}^{i+1} m_k} \qquad (i = 1, \cdots, n-1). \tag{2}$$

Let $\mathsf{W} \equiv (\boldsymbol{\rho}_1 \cdots \boldsymbol{\rho}_{n-1})$ be a $3 \times (n-1)$-dimensional matrix whose columns are the $(n-1)$ Jacobi vectors of the system. According to the singular-value decomposition theorem, the matrix W can be decomposed into the product of three matrices as

$$\mathsf{W} = \mathsf{RNU}^T, \tag{3}$$

where R is a three-dimensional orthogonal matrix whose three columns represent the instantaneous principal axes of the whole system. The matrix N is a $3 \times (n-1)$ "diagonal" matrix of the following structure,

$$\mathsf{N} = \begin{pmatrix} a_1 & 0 & 0 & 0 & \cdots & 0 \\ 0 & a_2 & 0 & 0 & \cdots & 0 \\ 0 & 0 & a_3 & 0 & \cdots & 0 \end{pmatrix}, \tag{4}$$

where the singular values a_1, a_2, and a_3 are the *gyration radii* of the system. Physically, the gyration radii represent the *mass distribution* of the system with respect to the three principal axes and are related to the three principal moments of inertia $M_1 \leq M_2 \leq M_3$ as

$$M_3 = a_1^2 + a_2^2, \; M_2 = a_1^2 + a_3^2, \; M_1 = a_2^2 + a_3^2. \tag{5}$$

That is,

$$a_1^2 = \frac{1}{2}(M_2 + M_3 - M_1), \quad a_2^2 = \frac{1}{2}(M_1 + M_3 - M_2), \quad a_3^2 = \frac{1}{2}(M_1 + M_2 - M_3). \quad (6)$$

The matrix U in Eq. (3) is an $(n-1) \times (n-1)$ orthogonal matrix of the form $\mathsf{U} \equiv (\boldsymbol{u}_1 \cdots \boldsymbol{u}_{n-1})$, where the $(n-1)$-dimensional vectors $\{\boldsymbol{u}_i\}$ are orthogonal to each other and normalized. In the framework of hyperspherical coordinates [14], the matrix U can be parametrized by the $(3n-9)$ hyperangles by restricting the matrix U to a subgroup of $O(n-1)$. Together with a_1, a_2, and a_3, these $(3n-6)$ variables in the matrices N and U are the internal coordinates that characterize the shape of the system uniquely, while the principal-axis frame R specifies the orientation of the whole system. The use of the $(3n-9)$ hyperangles generally makes the expression of kinetic energy highly involved. Instead, the use of $(3n-9)$ *quasivelocities* makes the expression of kinetic energy concise as summarized below.

Based on the singular-value decomposition in Eq. (3), the translation-reduced kinetic energy of the n-atom system can be generally expressed as

$$K = \frac{1}{2}\sum_{i=1}^{n-1} \dot{\boldsymbol{\rho}}_i \cdot \dot{\boldsymbol{\rho}}_i = K_{\rm rot} + K_{\rm int}. \quad (7)$$

Here, $K_{\rm rot}$ is the rotational kinetic energy given by

$$K_{\rm rot} = \frac{1}{2}\boldsymbol{L}^T \mathsf{M}^{-1} \boldsymbol{L}, \quad (8)$$

where $\boldsymbol{L}$ is a three dimensional vector of the angular momentum with respect to the principal-axis frame, and M is its corresponding 3×3 moment of inertia tensor. $K_{\rm int}$ is the internal kinetic energy and can be given explicitly as

$$\begin{aligned} K_{\rm int} &= \frac{1}{2}\left(\dot{a}_1^2 + \dot{a}_2^2 + \dot{a}_3^2\right) + \frac{\left(a_1^2 - a_2^2\right)^2}{2\left(a_1^2 + a_2^2\right)}\omega_{12}^2 + \frac{\left(a_2^2 - a_3^2\right)^2}{2\left(a_2^2 + a_3^2\right)}\omega_{23}^2 + \frac{\left(a_3^2 - a_1^2\right)^2}{2\left(a_3^2 + a_1^2\right)}\omega_{31}^2 \\ &\quad + \frac{1}{2}a_1^2\sum_{k=4}^{n-1}\gamma_{1k}^2 + \frac{1}{2}a_2^2\sum_{k=4}^{n-1}\gamma_{2k}^2 + \frac{1}{2}a_3^2\sum_{k=4}^{n-1}\gamma_{3k}^2, \end{aligned} \quad (9)$$

where $\{\omega_{ij}\}$ and $\{\gamma_{ik}\}$ are the *quasivelocities* defined by

$$\dot{\boldsymbol{u}}_i \cdot \boldsymbol{u}_j = -\boldsymbol{u}_i \cdot \dot{\boldsymbol{u}}_j \equiv \omega_{ij} \quad (i,j = 1,2,3, \quad i \neq j), \quad (10)$$

$$\dot{\boldsymbol{u}}_i \cdot \boldsymbol{u}_k = -\boldsymbol{u}_i \cdot \dot{\boldsymbol{u}}_k \equiv \gamma_{ik} \quad (i = 1,2,3, \quad k = 4,\ldots,n-1). \quad (11)$$

The vectors $\{\boldsymbol{u}_i\}$ are the $(n-1)$-dimensional vectors defined in the matrix U in Eq. (3). The quasivelocities $\{\omega_{ij}\}$ are anti-symmetric with respect to the exchange of the suffixes as $\omega_{ij} = -\omega_{ji}$. Both $\{\omega_{ij}\}$ and $\{\gamma_{ik}\}$ are the parts of the components of the $(n-1) \times (n-1)$ anti-symmetric matrix $\mathsf{U}^T\dot{\mathsf{U}}$, which is essentially an *internal angular velocity* associated with the shape changes of the system. We clarify the physical meanings of these quasivelocities in Section 4. Note that the expression Eq. (9) is valid for general n-atom ($n \geq 5$) systems. If $n \leq 4$, the quasivelocities $\{\gamma_{ik}\}$ do not exist, and all the terms

involving $\{\gamma_{ik}\}$ disappear from Eq. (9). Hereafter, we assume the general case of $n \geq 5$ unless otherwise noted.

An advantage of the expression Eq. (7) is that there is no Coriolis coupling term, and the partitioning of K into $K_{\rm rot}$ and $K_{\rm int}$ is independent of the choice of body frame. (It should be noted however that the terms on the right hand side of Eq. (9) have physical meanings specifically with respect to the principal-axis frame as will be clarified in Section 4.) When the total angular momentum of the system is zero, $\boldsymbol{L} = \mathbf{0}$, the rotational kinetic energy $K_{\rm rot}$ disappears and $K_{\rm int}$ is essentially the total kinetic energy of the system.

3 Hyperspherical modes

The internal kinetic energy Eq. (9) is remarkably simple in the sense that there is no cross term among the velocities of gyration radii $\{\dot{a}_i\}$ and the quasivelocities $\{\omega_{ij}\}$ and $\{\gamma_{ik}\}$. Moreover, the number of terms on the right-hand side of Eq. (9) is $(3n-6)$ in total, which is exactly the same as the number of internal degrees of freedom of the n-atom system. Therefore, it is tempting to consider the terms of Eq. (9) as the kinetic energies of respective $(3n-6)$ internal degrees of freedom. The first three terms proportional to $\dot{a}_1^2$, $\dot{a}_2^2$, and $\dot{a}_3^2$ are clearly the kinetic energies of the three gyration radii. But for the rest of the terms involving $\{\omega_{ij}\}$ and $\{\gamma_{ik}\}$, it is not as simple because one cannot attribute them to any coordinates since these quasivelocities are not derivatives of coordinates. Instead, these kinetic energies are the energies of respective *internal modes* characterized by the quasivelocities $\{\omega_{ij}\}$ and $\{\gamma_{ik}\}$ themselves.

Motivated by the concise expression of kinetic energy in Eq. (9), we clarify the physical meanings of the velocities $\{\dot{a}_i\}$ and quasivelocities $\{\omega_{ij}\}$ and $\{\gamma_{ik}\}$ and give the definitions for the corresponding hyperspherical modes. While the variables $\{\dot{a}_i\}$, $\{\omega_{ij}\}$ and $\{\gamma_{ik}\}$ in Eq. (9) are the *components* of a given velocity vector in the tangent space of the configuration space, the hyperspherical modes themselves are defined as the *basis vectors* conjugate to these components. Suppose that $\dot{\mathsf{W}}$ is a velocity vector of the system that satisfies the conditions of zero total angular momentum. Note that this $3\times(n-1)$ matrix $\dot{\mathsf{W}}$ can be regarded as a vector in the tangent space of the $(3n-3)$-dimensional translation-reduced configuration space by aligning all the columns of $\dot{\mathsf{W}}$ to a single column. As long as the vector $\dot{\mathsf{W}}$ satisfies the conditions of zero total angular momentum, $\dot{\mathsf{W}}$ can be expanded into $(3n-6)$ terms as

$$\dot{\mathsf{W}} = \sum_{i=1}^{3} \dot{a}_i \mathsf{V}_{a_i} + \sum_{ij=12,23,31} \omega_{ij} \mathsf{V}_{\omega_{ij}} + \sum_{i=1}^{3}\sum_{k=4}^{n-1} \gamma_{ik} \mathsf{V}_{\gamma_{ik}}, \tag{12}$$

where $\{\mathsf{V}_{a_i}\}$, $\{\mathsf{V}_{\omega_{ij}}\}$ and $\{\mathsf{V}_{\gamma_{ik}}\}$ are $3\times(n-1)$ matrices, which constitute the $(3n-6)$ basis vectors of this expansion. Each of these basis vectors corresponds to a hyperspherical mode. In what follows, we deduce the expressions for these basis vectors in a rather heuristic way.

We begin with the following expression for $\dot{\mathsf{W}}$,

$$\dot{\mathsf{W}} = \mathsf{R}\dot{\mathsf{N}}\mathsf{U}^T + \mathsf{R}\left(\Omega\mathsf{N} + \mathsf{N}\boldsymbol{\omega}^T\right)\mathsf{U}^T, \tag{13}$$

which is obtained from the time derivative of Eq. (3). In Eq. (13), the matrix $\Omega \equiv \mathsf{R}^T\dot{\mathsf{R}}$ is a 3×3 antisymmetric matrix corresponding to the angular velocity of the principal-

axis frame with respect to the principal-axis frame itself. The matrix $\boldsymbol{\omega} \equiv \mathsf{U}^T\dot{\mathsf{U}}$ is an $(n-1)\times(n-1)$ anti-symmetric matrix that can be expanded as

$$\boldsymbol{\omega} = \sum_{ij=12,23,31} \omega_{ij}\mathsf{X}_{ij} + \sum_{i=1}^{3}\sum_{k=4}^{n-1} \gamma_{ik}\mathsf{X}_{ik} + \sum_{k=4}^{n-2}\sum_{l=k+1}^{n-1} \gamma_{kl}\mathsf{X}_{kl}, \tag{14}$$

where X_{ij} are defined as the $(n-1)\times(n-1)$-dimensional antisymmetric matrix whose ij component is -1, ji component is $+1$, and all other components are zero. The matrices X_{ik} and X_{kl} have the similar structure, whose ik or kl component is -1 and ki or lk component is $+1$. In the first two terms on the right-hand side of Eq. (14), $\{\omega_{ij}\}$ and $\{\gamma_{ik}\}$ are the quasivelocities introduced in Eq. (10) and Eq. (11). In the third term of Eq. (14), we have introduced additional quasivelocities defined by

$$\dot{\boldsymbol{u}}_k \cdot \boldsymbol{u}_l = -\boldsymbol{u}_k \cdot \dot{\boldsymbol{u}}_l \equiv \gamma_{kl} \quad (k,l = 4,\cdots,n-1, \quad k<l). \tag{15}$$

The quasivelocities in Eq. (15) vanish after the matrix multiplication $\mathsf{N}\boldsymbol{\omega}^T$ in Eq. (13).

Our strategy here is to express Eq. (13) in the form of Eq. (12) and compare these two equations to deduce the basis vectors $\{\mathsf{V}_{a_i}\}$, $\{\mathsf{V}_{\omega_{ij}}\}$ and $\{\mathsf{V}_{\gamma_{ik}}\}$. So far, Eq. (13) is more general than Eq. (12) because Eq. (13) includes the situation that $\dot{\mathsf{W}}$ gives non-zero total angular momentum. Therefore, we need to assign the conditions of vanishing total angular momentum to Eq. (13). If the velocity vector $\dot{\mathsf{W}}$ in Eq. (13) satisfies the conditions of vanishing total angular momentum, one can eliminate the angular velocity of the principal-axis frame Ω by expressing it in terms of the internal variables only as is known from the gauge theory [10]. This can be done as follows.

The total angular momentum of the system (with respect to the space-fixed frame) for a given velocity vector $\dot{\mathsf{W}}$ can be expressed in the form of a 3×3 antisymmetric matrix as

$$\mathsf{L}_s = \dot{\mathsf{W}}\mathsf{W}^T - \mathsf{W}\dot{\mathsf{W}}^T. \tag{16}$$

By inserting Eq. (13) into Eq. (16), we obtain

$$\mathsf{L}_s = \mathsf{R}\left(\Omega\mathsf{N}\mathsf{N}^T + \mathsf{N}\omega^T\mathsf{N}^T - \mathsf{N}\mathsf{N}^T\Omega^T - \mathsf{N}\omega\mathsf{N}^T\right)\mathsf{R}^T. \tag{17}$$

Using this equation, the condition of vanishing total angular momentum, $\mathsf{L}_s = 0$, can be solved for Ω to give

$$\Omega = \begin{pmatrix} 0 & -\dfrac{2a_1a_2}{a_1^2+a_2^2}\omega_{12} & \dfrac{2a_3a_1}{a_3^2+a_1^2}\omega_{31} \\ \dfrac{2a_1a_2}{a_1^2+a_2^2}\omega_{12} & 0 & -\dfrac{2a_2a_3}{a_2^2+a_3^2}\omega_{23} \\ -\dfrac{2a_3a_1}{a_3^2+a_1^2}\omega_{31} & \dfrac{2a_2a_3}{a_2^2+a_3^2}\omega_{23} & 0 \end{pmatrix} \equiv \mathsf{A}_{12}\omega_{12} + \mathsf{A}_{23}\omega_{23} + \mathsf{A}_{31}\omega_{31} \tag{18}$$

where, in the final equality, A_{ij} $(ij = 12,23,31)$ are the 3×3 antisymmetric matrices whose ij components are $-2a_ia_j/(a_i^2+a_j^2)$, and ji components are $+2a_ia_j/(a_i^2+a_j^2)$ and all other components are zero. Physically, Eq. (18) is the angular velocity of the principal-axis frame that compensates for the angular momentum induced by the quasivelocities

ω_{12}, ω_{23} and ω_{31} to keep the total angular momentum to zero. After inserting Eq. (18) into Eq. (13) and using Eq. (14) for $\boldsymbol{\omega}$, we obtain a general expression for the velocity vector $\dot{\mathsf{W}}$ under the conditions of vanishing total angular momentum as

$$\dot{\mathsf{W}} = \sum_{i=1}^{3} \dot{a}_i \mathsf{R} \frac{\partial \mathsf{N}}{\partial a_i} \mathsf{U}^T + \sum_{ij=12,23,31} \omega_{ij} \mathsf{R} \left(\mathsf{A}_{ij} \mathsf{N} + \mathsf{N} \mathsf{X}_{ij}^T \right) \mathsf{U}^T + \sum_{i=1}^{3} \sum_{k=4}^{n-1} \gamma_{ik} \mathsf{R} \mathsf{N} \mathsf{X}_{ik}^T \mathsf{U}^T. \tag{19}$$

By comparing Eq. (19) with Eq. (12), we see that the three gyration-radius modes can be defined as

$$\mathsf{V}_{a_i} \equiv \mathsf{R} \frac{\partial \mathsf{N}}{\partial a_i} \mathsf{U}^T \quad (i = 1, 2, 3). \tag{20}$$

Similarly, the first three hyperangular modes corresponding to ω_{12}, ω_{23}, and ω_{31} can be defined as,

$$\mathsf{V}_{\omega_{ij}} \equiv \mathsf{R} \left(\mathsf{A}_{ij} \mathsf{N} + \mathsf{N} \mathsf{X}_{ij}^T \right) \mathsf{U}^T \quad (ij = 12, 23, 31), \tag{21}$$

and other hyperangular modes corresponding to $\gamma_{ik} (i = 1, 2, 3, k = 4, \cdots, n-1)$ can be defined as

$$\mathsf{V}_{\gamma_{ik}} \equiv \mathsf{R} \mathsf{N} \mathsf{X}_{ik}^T \mathsf{U}^T \quad (i = 1, 2, 3, \quad k = 4, \cdots, n-1). \tag{22}$$

Thus, Eqs. (20)-(22) give the definitions of the $(3n-6)$ internal modes. Note that the hyperspherical modes in Eqs. (20)-(22) are now expressed solely by the quantities that are obtained through the singular value decomposition in Eq. (3). Therefore, one can immediately compute all the hyperspherical modes through Eqs. (20)-(22) once the singular value decomposition Eq. (3) is obtained.

It can be shown that the hyperangular modes defined above are orthogonal to each other; in fact, we have

$$\mathrm{Tr} \left[\mathsf{V}_\alpha^T \mathsf{V}_\beta \right] = 0 \quad (\text{for } \alpha \neq \beta), \tag{23}$$

where α and β represent any of $\{a_i\}$, $\{\omega_{ij}\}$, and $\{\gamma_{ik}\}$. These orthogonal properties indicate that the hyperspherical modes form a set of orthogonal basis vectors that span the tangent space of the configuration space under the conditions of zero total angular momentum, which is a property similar to ordinary normal modes [23]. Furthermore, the hyperspherical modes are normalized to the coefficients of the kinetic energy in Eq. (9):

$$\mathrm{Tr} \left[\mathsf{V}_{a_i}^T \mathsf{V}_{a_i} \right] = 1 \quad (i = 1, 2, 3), \tag{24}$$

$$\mathrm{Tr} \left[\mathsf{V}_{\omega_{ij}}^T \mathsf{V}_{\omega_{ij}} \right] = \left(a_i^2 - a_j^2 \right)^2 / \left(a_i^2 + a_j^2 \right) \quad (ij = 12, 23, 31), \tag{25}$$

$$\mathrm{Tr} \left[\mathsf{V}_{\gamma_{ik}}^T \mathsf{V}_{\gamma_{ik}} \right] = a_i^2 \quad (i = 1, 2, 3, k = 4, \ldots, n-1). \tag{26}$$

Note that the kinetic energy of the system given in Eq. (7) can also be expressed as $2K = \mathrm{Tr} \left[\dot{\mathsf{W}}^T \dot{\mathsf{W}} \right]$. By inserting Eq. (12) into this kinetic energy expression, we can see that the orthonormal conditions, Eqs. (23)-(26), are vital to the concise expression of kinetic energy in Eq. (9) without any cross terms. Note finally that the hyperspherical modes are determined only by the quantities associated with kinetic energy, i.e., the atomic masses and the shape of the system, and are totally independent of the potential function of the system.

Equations (20)-(22) give the exact definitions of the $(3n-6)$ hyperspherical modes for an n-stom system. Kinetic energy in each hyperspherical mode is given as each term of

Eq. (9). We thus propose to use the concise expression of the kinetic energy Eq. (9) as a fundamental tool to investigate the intramolecular energy transfer in the dynamics of n-atom systems.

4 Representation of hyperspherical modes

We clarify here the physical meanings of respective hyperspherical modes defined in Eqs. (20)-(22) by taking an illustrative example of a six-atom Morse cluster. In this cluster, each pair of atoms interact through the pairwise Morse potential. This cluster possesses two local stable conformations (isomers) called OCT and CTBP, around which the 12 hyperspherical modes are shown in Fig. 1. Note that, in the hyperspherical mode analysis, the $(3n-6)$ internal modes of an n-atom molecule are generally classified into three *gyration-radius modes*, three *twisting modes*, and $(3n-12)$ *shearing modes* as was defined in Eqs. (20)-(22).

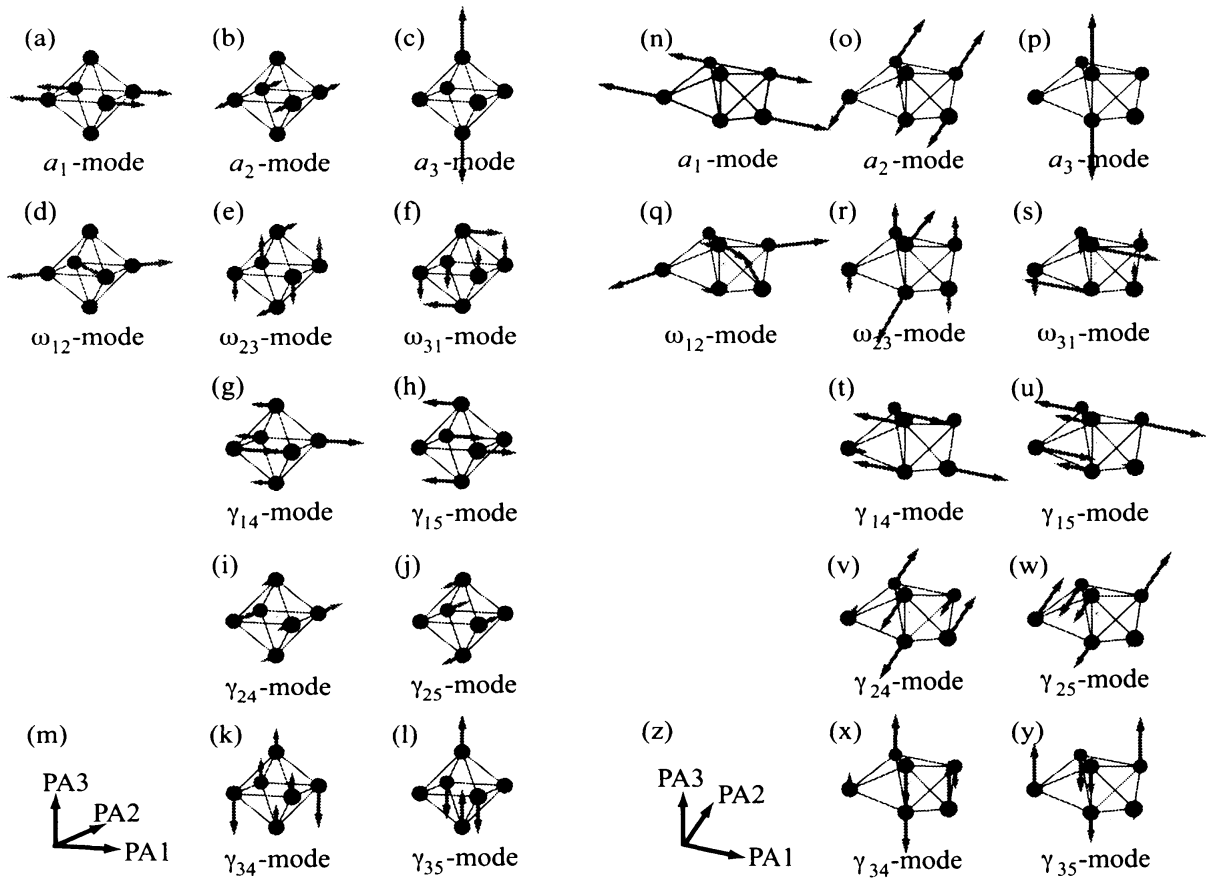

Figure 1: The twelve *hyperspherical modes* of the six-atom cluster, M_6, around the OCT ((a)-(l)) and the CTBP isomers ((n)-(y)). The cluster is aligned so that the first, second, and third principal axes (PA1, PA2, and PA3 respectively) are parallel to the axes indicated in (m) for OCT and in (z) for CTBP. (The OCT isomer shown here is slightly deformed from the potential energy minimum.)

From Fig. 1, we see the following properties for the respective hyperspherical modes. The three *gyration-radius modes*, a_1-,a_2-, and a_3-modes, shown in (a)-(c) and (n)-(p) for

the two isomers respectively, are related to the elongation and the contraction of the system along the three principal axes. For the three *twisting modes*, shown in (d)-(f) and (q)-(s), the arrows in each ω_{ij}-mode are perpendicular to the k-th ($k \neq i, j$) principal axis; one part of the system tends to rotate around the k-th principal axis in one direction, and the other part of the system tends to rotate in the opposite direction, giving rise to a twist around the k-th principal axis. The remaining six modes associated with γ_{ik} ($i = 1, 2, 3, k = 4, 5$), shown in (g)-(l) and (t)-(y), are the *shearing modes*; while all the atoms in each γ_{ik}-mode tend to move parallel to the i-th principal axis, some move in the positive direction and others move in the negative direction, giving rise to a shear in the system.

5 Trigger mechanisms for conformational transitions

By using the hyperspherical mode analysis summarized above, one can scrutinize the flow of kinetic energy among the hyperspherical modes in the conformational dynamics of complex molecular systems. Such information on the kinetic energy flow can in turn provide crucial information for understanding the mechanisms for large-amplitude collective motions. In the following, we summarize this procedure for the conformational transitions of the M_6 cluster between the OCT and CTCP isomers.

First, we have found that the gyration-radius modes acquire a large amount of energy in the course of the conformational transitions between the two isomers. Based on this fact, we have constructed a reaction coordinate a'_1, which is defined as a proper linear combination of the gyration-radius modes. The procedure for constructing the reaction coordinate a'_1 is detailed in Ref. [25]. In all of the figures in Fig. 2(a)-(d), the left region, where a'_1 is smaller than about 2.5, corresponds to the OCT isomer region, while the right region, where a'_1 is larger than about 2.5, corresponds to the CTBP isomer region. The coordinate a'_2 in Fig. 2(a) and (c) is a "bath" mode, which does not contribute to the conformational transition significantly, as opposed to the reaction coordinate a'_1.

Equations of motion for the gyration-radius modes have revealed that there are two kinds of forces acting on the coordinates a'_1 and a'_2: One is the potential force and the other is a kinematic force called internal centrifugal force (see Refs. [24, 25] for details). The internal centrifugal force originates from the kinematic couplings between the gyration-radius modes and other hyperspherical modes, i.e., the twisting modes and the shearing modes. The internal centrifugal force has an interesting property to distort a spherical mass distribution of a system into an elongated one, which is a symmetry breaking effect. As a result, the internal centrifugal force can be the driving force for the conformational transitions between a spherical isomer and an elongated isomer such as the transitions between OCT and CTBP of the M_6 cluster as we see in the following.

We have found that the internal centrifugal force changes very sensitively depending on the activity of the three twisting modes: Fig. 2(a) shows an averaged force field, which is the superposition of the averaged potential force and the averaged internal centrifugal force, under the condition that the three twisting modes are highly *active* having a large amount of kinetic energy. It is clearly seen from this figure that the force field has the strong tendency to accelerate (drive) the system from the OCT region into the CTBP

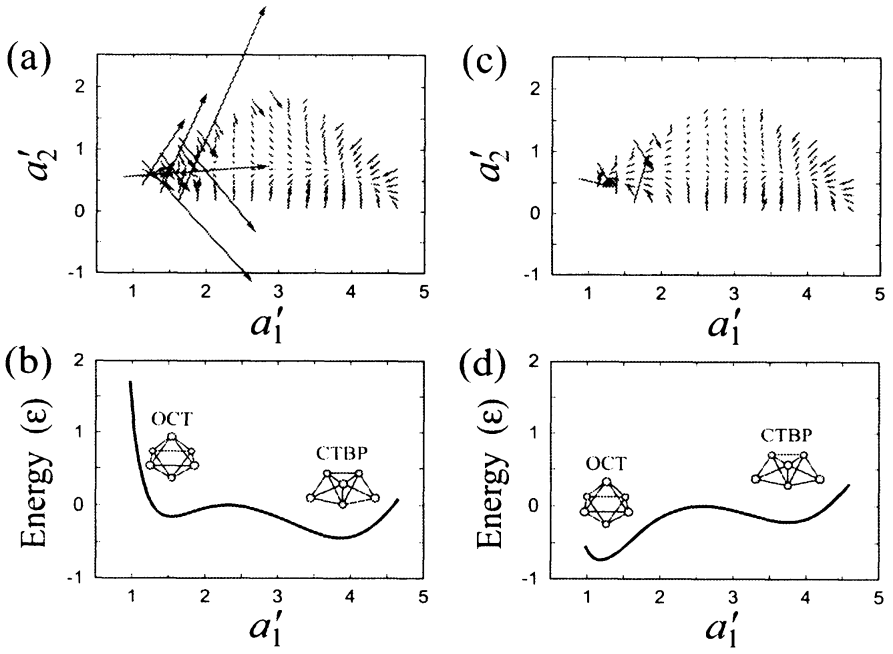

Figure 2: (a) Averaged force field in the space of the reaction coordinate a_1' and a "bath" mode a_2' when the three twisting modes are highly *active*. (b) Line integral (mean force potential) of the average force field in (a) along the reaction coordinate a_1'. (c) Average force field in the space of the reaction coordinate a_1' and a_2' when the three twisting modes are highly *inactive*. (d) Line integral (mean force potential) of the average force field in (c) along the reaction coordinate a_1'.

region along the reaction coordinate a_1'. This effect can also be characterized by the corresponding mean force potential, which is shown in Fig. 2(b). The results of Fig. 2(a) and (b) clearly show that the *activation* of the three twisting modes can be the principal factor to trigger the conformational transition from OCT to CTBP by making the OCT less favorable and CTBP more favorable. Indeed, we have confirmed that the three twisting modes of the cluster become highly *active* right before the onset of the conformational transition from OCT to CTBP [25].

In a similar way, we can understand the driving mechanism for the conformational transition from CTBP to OCT: Fig. 2(c) shows the average force field under the condition that the three twisting modes are highly *inactive*. This force field makes the OCT more favorable than CTBP, as can be more clearly seen from the corresponding mean force potential in Fig. 2(d). Thus, the results of Fig. 2(c) and (d) clearly show that the *inactivation* of the three twisting modes can be the principal factor to trigger the conformational transition from CTBP to OCT by making the CTBP less favorable and OCT more favorable. Indeed, we have confirmed that the three twisting modes of the cluster become highly *inactive* right before the onset of the conformational transition from CTBP to OCT [25].

Thus, the activation and inactivation of the twisting modes switch the effective force field in the reaction coordinate and control the onset of large amplitude collective motions. In this way, we have elucidated the trigger mechanisms for conformational transitions of the cluster by using the hyperspherical mode analysis.

6 Summary and concluding remarks

In this report, we have summarized the framework of hyperspherical mode analysis. This method has elucidated the novel trigger mechanisms for the onset of large-amplitude collective motions of atomic clusters.

In the hyperspherical mode analysis, the $(3n-6)$ internal (vibrational) modes of an n-atom system are classified generally into three gyration-radius modes, three twisting modes, and $(3n-12)$ shearing modes. Based on the fact that a large amount of kinetic energy flows into the gyration-radius modes when the conformational transitions take place, we have constructed a reaction coordinate as a linear combination of the three gyration-radius modes. It was then found that activation or inactivation of the three twisting modes, depending on the isomer of the cluster, play crucial roles right before the onset of conformational transition. In the symmetric isomer called OCT, which has a spherical mass distribution, activation of the twisting modes initiates the conformational transition into the other elongated isomer called CTBP by inducing a strong internal centrifugal force, which has an effect of elongating the mass distribution of the system. On the other hand, in the CTBP isomer, inactivation of the twisting modes initiates the conformational transition into the OCT isomer by suppressing the elongation effect of the internal centrifugal force and making the effects of the potential force dominant.

The roles of the twisting modes presented here is interesting from the viewpoint of *control* of conformational dynamics of molecules. As we have seen in Section 5, the elongation effect (symmetry breaking effect) of the internal centrifugal force depends critically on the activity of the twisting modes. Therefore, if one would like to synthesize or maintain molecular conformations with a spherical mass distribution, it would be important to keep the twisting modes inactive. On the other hand, if one would like to elongate and destroy molecular conformations with a spherical mass distribution, the twisting modes of the system should be activated. From this respect, it is interesting to study the roles of the twisting modes in the formation and dissociation of fullerenes and viral capsids, which generally have highly symmetric and spherical mass distributions. Study in this direction is under way.

Acknowledgments

This report is a summary of our previous joint work with Wang Sang Koon (Caltech) and Jerrold E. Marsden (Caltech). The author thanks for their valuable discussions and continued collaborations. The author also gratefully acknowledges the support from JSPS Fellowships for Research Abroad and JSPS Grant-in-Aid (Start-up).

References

[1] J. E. Marsden, R. Montgomery, and T. Ratiu, Contemp. Math. **28**, 101 (1984).

[2] J. E. Marsden and T. S. Ratiu, *Introduction to Mechanics and Symmetry* (Springer, New York, 1999).

[3] J. E. Marsden, T. S. Ratiu, and J. Scheurle, J. Math. Phys. **41**, 3379 (2000).

[4] M. Kummer, Indiana Univ. Math. J., **30**, 281 (1981).

[5] A. Guichardet, Ann. Inst. H. Poincaré **40**, 329 (1984).

[6] T. Iwai, J. Math. Phys. **28**, 964 (1987): **28**, 1315 (1987).

[7] T. Iwai, Ann. Inst. H. Poincaré **47**, 199 (1987).

[8] A. Tachibana and T. Iwai, Phys. Rev. A **33**, 2262 (1986).

[9] R. G. Littlejohn and M. Reinsch, Phys. Rev. A **52**, 2035 (1995).

[10] R. G. Littlejohn and M. Reinsch, Rev. Mod. Phys. **69**, 213 (1997).

[11] R. G. Littlejohn, K. A. Mitchell, V. A. Aquilanti, and S. Cavalli, Phys. Rev. A **58**, 3705 (1998).

[12] R. G. Littlejohn, K. A. Mitchell, M. Reinsch, V. Aquilanti, and S. Cavalli, Phys. Rev. A **58**, 3718 (1998).

[13] C. Eckart, Phys. Rev. **46**, 383 (1934).

[14] X. Chapuisat and A. Nauts, Phys. Rev. A **44**, 1328 (1991).

[15] X. Chapuisat, Phys. Rev. A **45**, 4277 (1992).

[16] A. Kuppermann, Adv. Mol. Vib. Col. Dyn. **2B**, 117 (1993).

[17] A. Kuppermann, J. Phys. Chem. **100**, 2621 (1996).

[18] A. Kuppermann, J. Phys. Chem. **101**, 6368 (1997).

[19] V. Aquilanti, A. Lombardi, and E. Yurtsever, Phys. Chem. Chem. Phys. **4**, 5040 (2002).

[20] V. Aquilanti, A. Lombardi, M. B. Sevryuk, and E. Yurtsever, Phys. Rev. Lett. **93**, 113402 (2004).

[21] V. Aquilanti, A. Lombardi, and M. B. Sevryuk, J. Chem. Phys. **121**, 5579 (2004).

[22] M. B. Sevryuk, A. Lombardi, and V. Aquilanti, Phys. Rev. A **72**, 033201 (2005).

[23] E. B. Wilson, Jr., J. C. Decius. and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

[24] T. Yanao, W. S. Koon, J. E. Marsden, and I. G. Kevrekidis, J. Chem. Phys. **126**, 124102 (2007).

[25] T. Yanao, W. S. Koon, and J. E. Marsden, J. Chem. Phys. **130**, 144111 (2009).