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Identification of almost invariant aggregates in reversible nearly uncoupled Markov chains

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Abstract

The topic of the present paper has been motivated by a recent computational approach to identify metastable chemical conformations and patterns of conformational changes within molecular systems. After proper discretization, such conformations show up as almost invariant aggregates in reversible, nearly uncoupled Markov chains (NUMCs). Most of the former work on this subject treated the *direct* problem: given the aggregates, analyze the loose coupling in connection with the computation of the stationary distribution (aggregation/disaggregation techniques). In contrast to that, the present paper focuses on the *inverse* problem: given the system as a whole, identify the almost invariant aggregates together with the (small) probabilities of transitions between them. A robust algorithm is worked out on the basis of some detailed perturbation analysis and illustrated at a simple molecular system.

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1. Introduction

The work to be presented here has been motivated by a recently suggested approach to identify and compute *metastable chemical conformations of biomolecules*. Given the physical characterization of such molecules in terms of their kinetic and potential energies, such conformations can be understood as *almost invariant subsets* of the related dynamical systems, see [1,2]. After discretization of a certain Markov operator, a finite-dimensional (time-homogeneous) Markov chain arises, which has the nice additional property of being *reversible*—i.e., symmetric with respect to time reversal. Per definition, every Markov chain with finite state space is associated with a *stochastic transition matrix*. Due to the reversibility of the Markov chain, the transition matrix is *symmetric* in some weighted l_2-sense. The new method involves the determination of conformations via the numerical solution and careful analysis of eigenvalue cluster problems around the so-called Perron root $\lambda = 1$, which characterizes the stochasticity of the transition matrix.

First, in Section 2, we start with a recollection of known basic results for reversible *uncoupled* Markov chains (UMCs) in terms of some block structure of their associated transition matrices. We introduce some weighted l_2-product and derive a discriminating sign structure for the identification of *invariant aggregates*, the finite-dimensional analog of invariant subsets that characterize the conformations to be determined. Next, in Section 3, we treat the case of *nearly uncoupled* Markov chains, wherein only a perturbed block structure is present, which is even hidden due to some unknown permutation. In addition, the number k of blocks is a priori unknown and must be determined. This case is first studied in terms of a linear *perturbation analysis* for the transition matrix (Section 3.1). In order to define "small" perturbations, coupling measures between aggregates are discussed (Section 3.2). On this basis, we derive a robust identification algorithm in Section 4. Part of the algorithm has been transformed into a *graph coloring* problem, which is known to be NP-complete. As a consequence, heuristics are justified to play an important role in the implementation of the algorithm. Finally, in Section 5, numerical experiments for simple model problems are illustrated.

2. Markov chains and transition matrices

For the convenience of the reader, we first recollect basic results about the connection between finite-dimensional Markov chains and their related transition matrices. This involves the stochastic characterization as well as its linear algebra counterpart.

2.1. Properties of transition matrices

Let the (row) *stochastic* (n, n)-matrix $P = (p_{ij})$ be a *transition matrix* associated with a (homogeneous) *Markov chain* over some finite set $\mathcal{S} = \{s_1, \ldots, s_n\}$ of

discrete states s_i. Given that the dynamical system is in the individual state s_i, each matrix entry p_{ij} represents the probability of the system to move to state s_j. For a more detailed understanding of Markov chains and their interpretation, we refer to textbooks like [3]. Throughout this paper, we will assume that P is *primitive*, i.e., there exists a positive integer m such that $P^m > 0$ elementwise [3]. Primitive stochastic matrices have some nice properties, which we recall now.

Theorem 2.1 [3,4]. *Let P be a primitive stochastic matrix. Then:*
1. *the Perron root $\lambda = 1$ is simple and dominant, i.e., $|\lambda| < 1$ for any other eigenvalue $\lambda \neq 1$,*
2. *there are positive left and right eigenvectors corresponding to $\lambda = 1$, which are unique up to constant multiples.*

In particular, the *right* eigenvector corresponding to $\lambda = 1$ is $e = (1, \ldots, 1)^{\mathrm{T}}$, the corresponding *left* eigenvector $\pi = (\pi_1, \ldots, \pi_n)^{\mathrm{T}}$ represents the *stationary distribution* under the assumption that $\pi^{\mathrm{T}} e = 1$ is chosen as normalization. In matrix notation we have

$$\pi^{\mathrm{T}} P = \pi^{\mathrm{T}} \quad \text{and} \quad Pe = e.$$

From our application context [2], the eigenvector π is given a priori. Moreover, the underlying Markov chains are known to be *reversible* so that the so-called *detailed balance condition* holds

$$\pi_i p_{ij} = \pi_j p_{ji} \quad \text{for all } i, j \tag{1}$$

or, in terms of some *weighting matrix* $\mathscr{D} = \mathrm{diag}(\sqrt{\pi_i})$, equivalently

$$\mathscr{D}^2 P = P^{\mathrm{T}} \mathscr{D}^2. \tag{2}$$

Throughout the subsequent analysis, we will conveniently assume that the discrete states have been selected such that *all* elements of π are strictly positive or, equivalently, that the weighting matrix D is non-singular. If this assumption were not satisfied in practice, one would just have to restrict the state space $\mathscr{S}$ accordingly. Once $\pi > 0$, we may introduce the inner product $\langle \cdot, \cdot \rangle_\pi$ as

$$\langle x, y \rangle_\pi = x^{\mathrm{T}} \mathscr{D}^2 y.$$

This inner product corresponds to the finite-dimensional *weighted* Euclidean space $l^2_\pi(n)$. Two vectors x, y satisfying $\langle x, y \rangle_\pi = 0$ will be called *π-orthogonal*.

Proposition 2.2. *Let P be a reversible primitive stochastic matrix. Then P is symmetric with respect to the inner product $\langle \cdot, \cdot \rangle_\pi$.*

Proof. Due to (2), we immediately have $\langle x, Py \rangle_\pi = x^{\mathrm{T}} \mathscr{D}^2 P y = x^{\mathrm{T}} P^{\mathrm{T}} \mathscr{D}^2 y = \langle Px, y \rangle_\pi$. □

The stochastic matrix P possesses the following structural properties:

P.1 There exists a basis of π-orthogonal right eigenvectors, which diagonalizes P.

P.2 All eigenvalues of P are real and contained in the interval $[-1, +1]$.

P.3 For every *right* eigenvector x there is an associated *left* eigenvector $y = \mathscr{D}^2 x$, which corresponds to the same eigenvalue.

P.4 The matrix P is similar to the symmetric, in general non-stochastic matrix $P_{\text{sym}} = \mathscr{D} P \mathscr{D}^{-1}$ (see also [5]).

2.2. Uncoupled Markov chains

As a generalization of transition probabilities between single states s_i we will need to define transition probabilities between non-void subsets of state space, usually called *aggregates*.

Definition 2.3. Given a Markov chain by its transition matrix P (not necessarily primitive) and a stationary distribution $\pi > 0$. Given any non-empty index subset I, define its characteristic vector $e_I = (e_{I,i})_{i=1,\ldots,n}$ by $e_{I,i} = 1$ for $i \in I$ and $e_{I,i} = 0$ otherwise. Identify index sets A and B with their two corresponding aggregates A and B. Then the (conditional) *transition probability* from A to B with respect to π is defined to be the conditional probability of the system being in A to move to B in a single step, which is given by

$$w_\pi(A, B) = \frac{\sum_{a\in A, b\in B} \pi_a \, p_{ab}}{\sum_{a\in A} \pi_a} = \frac{\langle e_B, P e_A\rangle_\pi}{\langle e_A, e_A\rangle_\pi}.$$

Definition 2.4 [7,8]. Let $A_1, \ldots, A_k$ denote a disjoint decomposition of the state space into k aggregates. Then the associated stochastic (k, k)-matrix W_π defined by

$$(W_\pi)_{ij} = w_\pi(A_i, A_j), \quad i, j = 1, \ldots, k,$$

is called the *coupling matrix* of the decomposition.

For the special case $A = B$, we call $w_\pi(A, A)$ the *probability for the system to stay within A*. An aggregate A satisfying $w_\pi(A, A) = 1$ is said to be *invariant*, which means that whenever the dynamical system is in A, it will remain in A *for infinite time*. A Markov chain is called *uncoupled*, if it allows the state space to be decomposed into disjoint invariant aggregates $A_1, \ldots, A_k$, i.e.,

$$w_\pi(A_i, A_j) = \delta_{ij} \quad \text{or} \quad W_\pi = \mathrm{Id}_k. \tag{3}$$

Formally speaking, the stationary distribution in this case is not unique, since the corresponding transition matrix is not primitive. The probabilities, however, are independent of any choice of stationary distribution. On the side of the transition matrix P, a UMC with k aggregates—assuming appropriate ordering of states—shows up in some *block-diagonal* form

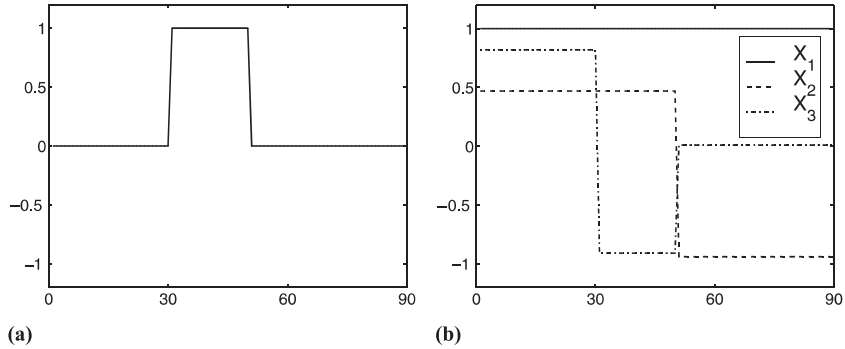

Fig. 1. Uncoupled Markov chain with $k = 3$ aggregates. The state space $\{s_1, \ldots, s_{90}\}$ divides into the aggregates $A_1 = \{s_1, \ldots, s_{29}\}$, $A_2 = \{s_{30}, \ldots, s_{49}\}$ and $A_3 = \{s_{50}, \ldots, s_{90}\}$. (a) Characteristic function χ_{A_2}. (b) A possible basis of the eigenspace corresponding to $\lambda = 1$. Observe that each eigenvector is constant on each aggregate. The sign structure for state s_{69} is $(+, -, 0)$ in the sense of Lemma 2.5.

$$P = D = \begin{pmatrix} D_{11} & 0 & \cdots & 0 \\ 0 & D_{22} & \cdots & 0 \\ \cdot & \cdot & & \cdot \\ 0 & 0 & \cdots & D_{kk} \end{pmatrix}, \tag{4}$$

where each block D_{ii} is a square *stochastic* matrix, *symmetric* with respect to some corresponding stationary subdistribution. Assume again that each of these matrices D_{ii} is *primitive*. Then, due to the Perron–Frobenius theorem, each block D_{ii} possesses a unique eigenvector $e_i = (1, \ldots, 1)^{\mathrm{T}}$ of length $\dim(D_{ii})$ corresponding to its Perron root $\lambda_i = 1$. Therefore, in terms of the total transition matrix P, the eigenvalue $\lambda = 1$ is k-fold and the corresponding eigenspace is spanned by the vectors

$$\chi_{A_i} = (0, \ldots, 0, e_i^{\mathrm{T}}, 0, \ldots, 0)^{\mathrm{T}}, \quad i = 1, \ldots, k.$$

In view of the inverse problem to be treated, our notation deliberately emphasizes that these eigenvectors can be interpreted as *characteristic functions* of the invariant aggregates (see Fig. 1(a)). In general, any basis $\{X_i\}_{i=1,\ldots,k}$ of the eigenspace corresponding to $\lambda = 1$ can be written as a linear combination of the characteristic functions χ_{A_i} with coefficients $\alpha_{ij} \in \mathbf{R}$ such that

$$X_i = \sum_{j=1}^{k} \alpha_{ij}\, \chi_{A_j}, \quad i = 1, \ldots k. \tag{5}$$

As a consequence, eigenvectors corresponding to $\lambda = 1$ are *constant on each aggregate* (see Fig. 1(b)).

With these preparations, we are now ready to derive the key tool for our algorithm to be presented in Section 4.

Lemma 2.5. *Given a block-diagonal transition matrix P consisting of reversible, primitive blocks, a stationary distribution $\pi > 0$ and a π-orthogonal basis*

$\{X_i\}_{i=1,\dots,k}$ of its eigenspace corresponding to $\lambda = 1$. Associate with every state s_i its sign structure

$$s_i \longmapsto (\mathrm{sign}((X_1)_i), \dots, \mathrm{sign}((X_k)_i)). \tag{6}$$

Then:

1. *invariant aggregates are collections of states with common sign structure*,
2. *different aggregates exhibit different sign structures.*

Proof. In order to prove statement 1, recall that each eigenvector corresponding to $\lambda = 1$ is constant on each of the aggregates, which implies that states belonging to the same aggregate must share the same sign structure.

As for statement 2, let, without loss of generality, every aggregate consists of only one state. In a first step, we demonstrate the assertion for an orthogonal eigenvector basis $\{Q_i\}_{i=1,\dots,k}$ of the symmetric matrix $P_{\mathrm{sym}} = \mathscr{D}P\mathscr{D}^{-1}$ (Property P.4). In a second step, we then generalize it to the assertion stated in the proposition.

Define the $k \times k$ matrix $Q = [Q_1 \cdots Q_k]$. Since Q is orthogonal, i.e., $Q^{\mathrm{T}} = Q^{-1}$, the transpose Q^{T} is an orthogonal matrix, too. Thus, the rows of Q are orthogonal, a fact that we will exploit in the following.

Now consider a π-orthogonal eigenvector basis $\{X_i\}_{i=1,\dots,k}$ of P. Then $X_i = \mathscr{D}^{-1}Q_i$ for $i = 1, \dots, k$. Since the transformation matrix $\mathscr{D}^{-1}$ has positive diagonal entries, the sign structures of X_i and Q_i, $i = 1, \dots, k$, are the same.

In view of Property P.4, the sign structure of the mth aggregate is equal to the sign structure of the mth row of $X = [X_1 \cdots X_k]$. Now suppose there exist two aggregates A_i and A_j with the same sign structure. Then the ith and jth row of X, and thus of Q, are equal in sign, which is a contradiction to the orthogonality of Q. □

Summarizing, Lemma 2.5 indicates that the set of k right eigenvectors associated with the k-fold eigenvalue $\lambda = 1$ can be conveniently used to *identify* k invariant aggregates *via sign structures*—to be tested *componentwise* and therefore independent of any (unknown) permutation. In principle, this testing could be performed via *left* as well as via *right* eigenvectors, whose sign structures are known to be the same. Just recall that for every left eigenvector $y = (y_i)$ there exists an associated right eigenvector $x = (x_i)$ with $y_i = \pi_i x_i$, hence $\mathrm{sign}(y_i) = \mathrm{sign}(x_i)$. Due to their constant level structure, however, the right eigenvectors seem to be better suited in view of a treatment of inverse problems in the presence of perturbations, which will be treated in the following section.

3. Nearly uncoupled Markov chains (NUMCs)

In most real life applications including those from molecular dynamics, perturbations occur that give rise to *nearly uncoupled* rather than UMCs—corresponding to

a decomposition into *invariant* rather than invariant aggregates. Roughly speaking, whenever the dynamical system is within a nearly invariant aggregate, then it will stay there *for a long time* rather than for infinite time—hence *metastability* rather than stability is the term to describe this situation. On the side of the transition matrices, *block-diagonally dominant* rather than block-diagonal matrices will occur. As will turn out, right eigenvectors of P can again be used to identify such aggregates—based on some subtle perturbation analysis to be given first.

3.1. Perturbation analysis

The theoretical perturbation analysis to be worked out in this section rather closely follows the lines of work of Stewart [8] on general primitive stochastic matrices. However, we additionally exploit *reversibility* of the Markov chain here using the framework prepared in Section 2. In the perturbed situation to be tackled now, the stationary distribution π of the transition matrix is unique, so that the inner product with respect to π is well defined. We may therefore drop the subscript π and just write $w(A, B) = w_\pi(A, B)$ for the probabilities and $W = W_\pi$ for the coupling matrix. For our perturbation analysis, we will employ the well-known theory of Kato [9], specified here to the case of *symmetric* matrices in the sense of Proposition 2.2.

Recall from (3) that an invariant aggregate A is defined by $w(A, A) = 1$. Therefore, again roughly speaking, an aggregate A will be said to be *almost invariant*, if $w(A, A) \approx 1$. In a similar way, a Markov chain will be called *nearly uncoupled*, if its state space can be decomposed into k disjoint *almost invariant* aggregates $A_1, \ldots, A_k$ such that

$$w(A_i, A_j) \approx \delta_{ij} \quad \text{or} \quad W \approx \mathrm{Id}_k. \tag{7}$$

In this situation, the states of an NUMC with k aggregates *can be ordered* such that the transition matrix P is of *block-diagonally dominant* form

$$P = D + E = \begin{pmatrix} D_{11} & E_{12} & \cdots & E_{1k} \\ E_{21} & D_{22} & \cdots & E_{2k} \\ \cdot & \cdot & & \cdot \\ E_{k1} & E_{k2} & \cdots & D_{kk} \end{pmatrix}. \tag{8}$$

Herein the perturbation matrix E is understood to satisfy $E = \mathrm{O}(\epsilon)$ in terms of some perturbation parameter ϵ to be further specified in Section 3.2. For the time being, we just want to analyze the underlying block-diagonally dominant structure as a function of this perturbation parameter. Let $P(\epsilon)$ be a family of matrices and define ϵ_* such that $P(\epsilon_*) = P$. Note that in our application context not only the actual size of ϵ_* will be *unknown*, but also the number k of blocks in the representation (8). Both of these aspects depend on the choice of criteria to measure *weak coupling* between aggregates—a topic left to Section 3.2. In order to be able to perform our linear perturbation analysis, we adopt from [9] the following technical assumptions.

Regularity conditions (*RC*). In accordance with Theorem 6.1 from [9], let

$$P(\epsilon) = P(0) + \epsilon P^{(1)} + \epsilon^2 P^{(2)} + \cdots$$

be a family of matrices that is analytic in a domain of the complex plane containing the origin, such that $P(\epsilon)$ is reversible and stochastic for real ϵ. Furthermore, let $P(\epsilon)$ be primitive for real $\epsilon \neq 0$ and $P(0)$ of block-diagonal form (4) with primitive blocks D_{ii}, $i = 1, \ldots, k$. By Theorem 2.1 each $P(\epsilon)$ admits a unique *positive* stationary distribution $\pi(\epsilon)$. We assume the set of all $\pi(\epsilon)$ to be uniformly bounded away from zero, i.e., there exists a constant $C > 0$ such that $\pi_i(\epsilon) \geqslant C$ for $i = 1, \ldots, n$ and real ϵ including $\epsilon = 0$.

These regularity conditions assure that, for sufficiently small $\epsilon \in \mathbf{R}$, the eigenvalues are continuous in ϵ and the spectrum of $P(\epsilon)$ can be divided into three parts [7–9]:

1. the Perron root $\lambda_1(\epsilon) \equiv 1$,
2. a cluster of $k - 1$ eigenvalues $\lambda_2(\epsilon), \ldots, \lambda_k(\epsilon)$ that approach 1 for $\epsilon \to 0$, and
3. the remaining part of the spectrum, which is bounded away from 1 for $\epsilon \to 0$.

In other words: For sufficiently small real ϵ, there exists a well-identifiable cluster of k eigenvalues around the Perron root—to be called *Perron cluster* herein—that may be understood as the splitting of a k-fold Perron root under perturbation. The following theorem gives a characterization of the eigenvectors $X_1(\epsilon), \ldots, X_k(\epsilon)$ corresponding to the Perron cluster.

Theorem 3.1. *Let $P(\epsilon)$ be a family of matrices satisfying the regularity conditions (RC). Let Π_j denote the π-orthogonal projection on the eigenspace spanned by the eigenvector X_j of the unperturbed transition matrix $P(0)$. Then, for real ϵ, there exist π-orthonormal eigenvectors $X_1(\epsilon), \ldots, X_k(\epsilon)$ of the following form*:

(i) *An eigenvector corresponding to the Perron root $\lambda_1(\epsilon) \equiv 1$ given by*

$$X_1(\epsilon) \equiv (1, \ldots, 1)^{\mathrm{T}},$$

(ii) *A set of $k - 1$ eigenvectors corresponding to the eigenvalue cluster $\lambda_2(\epsilon), \ldots, \lambda_k(\epsilon)$ near $\lambda = 1$ of the form*

$$X_i(\epsilon) = \sum_{j=1}^{k} \alpha_{ij} \chi_{A_j} + \epsilon X_i{}^{(1)} + \mathrm{O}(\epsilon^2) \tag{9}$$

with

$$X_i{}^{(1)} = \sum_{j=1}^{k} \beta_{ij} \chi_{A_j} + \sum_{j=k+1}^{n} \frac{1}{1 - \lambda_j} \Pi_j P^{(1)} X_i \tag{10}$$

for appropriate coefficients $\alpha_{ij}, \beta_{ij} \in \mathbf{R}$ and aggregates $A_1, \ldots, A_k$ corresponding to the block-diagonal form of $P(0)$.

Proof. Since $P(\epsilon)$ is primitive for real $\epsilon \neq 0$, the eigenvalue $\lambda_1(\epsilon) \equiv 1$ is simple for real $\epsilon \neq 0$. The corresponding left-eigenvector $\pi(\epsilon)$, the stationary distribution, is positive and analytic for real ϵ [9, Theorem II.2.3]. Define the transformation matrix $\mathscr{D}(\epsilon) = \mathrm{diag}(\sqrt{\pi_i(\epsilon)})$; since the $\pi(\epsilon)$ are "uniformly bounded away from

zero", $\mathscr{D}(\epsilon)$ is invertible for real ϵ. The transformed family of matrices $P_{\mathrm{sym}}(\epsilon) = \mathscr{D}(\epsilon)P(\epsilon)\mathscr{D}(\epsilon)^{-1}$ is analytic in ϵ and symmetric for real ϵ (consequence 2.1 of Proposition 2.2).

By [9, Section II.6.2] there exist right eigenvectors $Y_1(\epsilon), \ldots, Y_k(\epsilon)$ of $P_{\mathrm{sym}}(\epsilon)$ corresponding to the eigenvalues $\lambda_1(\epsilon), \ldots, \lambda_k(\epsilon)$, which are analytic for real ϵ. Transforming these vectors by $\mathscr{D}(\epsilon)^{-1}$, we see that $X_i(\epsilon) = \mathscr{D}(\epsilon)^{-1}Y_i(\epsilon)$, the corresponding eigenvectors for the reversible matrices $P(\epsilon)$, are analytic for real ϵ and therefore admit an expansion in ϵ: $X_i(\epsilon) = X_i + \epsilon X_i{}^{(1)} + \mathrm{O}(\epsilon^2)$.

Now, let $\Pi(\epsilon) = \Pi_1(\epsilon) + \cdots + \Pi_k(\epsilon)$ denote the π-orthogonal projection on the eigenspace of $P(\epsilon)$ corresponding to the eigenvalues $\lambda_1(\epsilon), \ldots, \lambda_k(\epsilon)$. Then, by [9, Section II.2.1], $\Pi(\epsilon)$ is analytic in ϵ and

$$\Pi(\epsilon) = \Pi(0) + \epsilon \sum_{j=k+1}^{n} \frac{1}{1-\lambda_j} \Big(\Pi(0)P^{(1)}\Pi_j + \Pi_j P^{(1)}\Pi(0) \Big) + \mathrm{O}(\epsilon^2).$$

Plugging $X_i(\epsilon) = X_i + \epsilon X_i{}^{(1)} + \mathrm{O}(\epsilon^2)$ into the identity $X_i(\epsilon) = \Pi(\epsilon)X_i(\epsilon)$ for $i = 1, \ldots, k$, one obtains

$$X_i{}^{(1)} = \sum_{j=1}^{k} \tilde{\beta}_{ij} X_j + \sum_{j=k+1}^{n} \frac{1}{1-\lambda_j} \Pi_j P^{(1)} X_i$$

for appropriate coefficients $\tilde{\beta}_{ij} \in \mathbf{R}$. Using Eq. (5) then completes the proof. □

Combining Eqs. (9) and (10), the first order perturbation result from Theorem 3.1

$$X_i(\epsilon) = \underbrace{\sum_{j=1}^{k} (\alpha_{ij} + \epsilon\, \beta_{ij})\, \chi_{A_j}}_{\text{(I)}} + \underbrace{\epsilon \sum_{j=k+1}^{n} \frac{1}{1-\lambda_j} \Pi_j P^{(1)} X_i + \mathrm{O}(\epsilon^2)}_{\text{(II)}} \tag{11}$$

permits an intriguing observation: The terms (I) are just shifts (up or down) of the locally constant levels to be associated with the almost invariant aggregates. This part of the error will not spoil the sign structure. The terms (II), however, which are of the form $\epsilon B + \mathrm{O}(\epsilon^2)$, can pollute the constant level pattern to some extent, but may affect the sign structure from Lemma 2.5 only to a smaller extent—with caution to be taken with respect to the perturbation of any "almost zero" levels (for details see Section 4). The above two parts of the perturbation permit a further interpretation in terms of the "weak modes" X_i, $i = k+1, \ldots, n$, and the "dominant modes" X_i, $i = 1, \ldots, k$: the term (I) represents the "dominant–dominant" coupling, whereas the terms (II) represent the "weak–dominant" coupling terms. Finally, observe that the terms (II) depend dominantly on the spectral gap $1 - \lambda_{k+1}$ between the Perron root and the remaining part of the spectrum, but not on the spectral gap $\lambda_k - \lambda_{k+1}$ between the Perron cluster and the rest.

3.2. Weak coupling between aggregates

We now turn to the important question of how to define the perturbation parameter ϵ more precisely than just by the vague assumption (7). As soon as the k almost-invariant aggregates have been computed, the (k, k) coupling matrix W can be computed as well from its Definition 2.3. On this basis, we will call a Markov chain *nearly uncoupled*, if

$$\|W - \mathrm{diag}(W)\|_\infty = 1 - \min_i w(A_i, A_i) = \epsilon_* \tag{12}$$

with the notation $\mathrm{diag}(W) = \mathrm{diag}(w_{11}, \ldots, w_{kk})$ and for "sufficiently small" $\epsilon_* > 0$ (compare the previous definition $P(\epsilon_*) = P$). This implies that perturbations of the transition matrix (8) are then characterized by

$$\|\mathscr{D}^2 E\|_\infty \leqslant \epsilon_* \tag{13}$$

with $\mathscr{D} = \mathrm{diag}(\sqrt{\pi_i})$ the weighting matrix as in Section 2.2. The above upper bound (13) may be easily verified using Definition 2.3 and relation (12).

Remark. Our characterization of NUMCs is different from the *uncoupling measure* of Hartfiel and Meyer [10], but related to the concept of the *conductance* of a Markov chain of Sinclair [11].

With this specification, we now return to the identification process. As already stated at the end of Section 3.1, we want to exploit the sign structure on the theoretical basis of the above the perturbation results. Assume that the identification process via the sign structure has supplied certain aggregates $A_1, \ldots, A_k$, suspected to be almost invariant. Upon using the $n \times k$ matrices $\chi = [\chi_{A_1} \cdots \chi_{A_k}]$ and $X = [X_1 \cdots X_k] = X(\epsilon)$, the perturbation result (11) may be expressed in view of actual computation as

$$X = \chi \mathscr{A}^{-1} + \epsilon B + \mathrm{O}(\epsilon^2)$$

with a $k \times k$ coefficient matrix $\mathscr{A} = \mathscr{A}(\epsilon)$ and an $n \times k$ matrix B representing the "weak–dominant" coupling terms (II) from (11). In view of the underlying perturbation theory, we may determine a non-singular coefficient matrix $\mathscr{A} = (a_{ij})$ by means of the *least squares fit*

$$\left\| \chi_{A_i} - \sum_{j=1}^{k} a_{ji} X_j \right\|_\pi = \text{min!} \quad \text{for all } i = 1, \ldots, k \tag{14}$$

in the weighted norm $\|\cdot\|_\pi$ introduced in Section 2.

Next, with the notation $\Lambda = \mathrm{diag}(\lambda_1, \ldots, \lambda_k) = \Lambda(\epsilon)$ for the Perron cluster of eigenvalues, the coupling matrix can be written as

$$W = (\chi^{\mathrm{T}} \mathscr{D}^2 \chi)^{-1} (\chi^{\mathrm{T}} \mathscr{D}^2 P \chi) = \mathscr{A}^{-1} \Lambda \mathscr{A} + \epsilon \Delta.$$

Again, the term $\mathscr{A}^{-1} \Lambda \mathscr{A}$ describes the "dominant–dominant" interaction, whereas the matrix Δ represents the "weak–dominant" interaction given by

$$\Delta = X^{\mathrm{T}}\mathscr{D}^2 B\Lambda - \Lambda B^{\mathrm{T}}\mathscr{D}^2 X + \mathrm{O}(\epsilon).$$

Recall that, in the case of an *uncoupled* Markov chain, we had $B = 0$ and $\Lambda = \mathrm{Id}_k$, implying $\Delta = 0$ and $W = \mathscr{A}^{-1}\Lambda\mathscr{A} = \mathrm{Id}_k$. For the nearly uncoupled Markov chains under consideration here, we may expect $\mathscr{A}^{-1}\Lambda\mathscr{A} \approx \mathrm{Id}_k$ and therefore interpret the $k \times k$ matrix

$$\mathrm{err}(A_1, \ldots, A_k) = \epsilon\Delta = W - \mathscr{A}^{-1}\Lambda\mathscr{A} \tag{15}$$

as *error indicator*. Recall from the perturbation analysis in Section 3.1 that this indicator measures the coupling of the weak modes to the dominant modes, i.e., it measures that part of the coupling which *cannot* be described in terms of the eigenspace of the Perron cluster. If an entry of $\mathrm{err}(A_1, \ldots, A_k)$ is large, this may be caused by one of the following reasons:

1. The value ϵ_* might be "not small enough" to permit the linear perturbation analysis.
2. The regularity conditions might be violated.
3. Our identification algorithm might have supplied "wrong" almost invariant aggregates—a phenomenon which may occur, if the perturbations had crucially spoiled the sign structure. Of course, there is an overlap with the first reason above.

4. Identification algorithm

In this section, we present details of implementation of our algorithm for the identification of almost invariant aggregates. Recall the *key algorithmic idea* to be worked out: *identify almost invariant aggregates componentwise via the sign structure of the eigenvectors corresponding to the Perron cluster of eigenvalues.*

First, we have to determine the *number k of almost invariant aggregates*. This is done by computing a cluster of eigenvalues near $\lambda = 1$, the Perron cluster, which should be well separated from the remaining part of the spectrum by a gap (Theorem 3.1). Iterative eigenvalue solvers with simultaneous subspace iteration (see e.g. [12] or [6, Section 4]) would be the natural way to perform this task. In our present version of the algorithm, however, we simply apply a direct eigenvalue solver to calculate all eigenvalues and split off a Perron cluster by examination. Second, once the $k - 1$ right Perron eigenvectors (apart from the already known eigenvector e) have been computed, we want to decompose the state space into k almost invariant aggregates. As worked out in Section 2.2 for *uncoupled* Markov chain, this can be done by exploiting the eigenvectors in terms of their "piecewise constant level" structure or their sign structure. However, for *NUMCs*, both perturbations of the eigenvectors and permutations may cover these structures to an unknown extent. This makes the construction of an efficient identification algorithm a quite subtle task. In what follows, we will describe the three main steps of our suggested algorithm.

Step 1. *Select states with stable sign structure*. We start from the heuristics that the *sign* of an eigenvector component is the "more likely" to remain stable under

perturbation, the "larger" this component is. This means that we are particularly interested in all those states $s \in \{1, \ldots, n\}$, for which at least one of the eigenvectors X_i has a "significantly large" component $X_i(s)$. In order to make the positive and negative parts of the different eigenvectors comparable in size, we scale them as follows: for $i = 1, \ldots, k$, we split $X_i = X_i^+ + X_i^-$ componentwise, where $X_i^+(s) = \max(0, X_i(s))$ and $X_i^-(s) = \min(0, X_i(s))$, and set $\tilde{X}_i = X_i^+/\|X_i^+\|_\infty + X_i^-/\|X_i^-\|_\infty$. This procedure leaves the eigenvector for $\lambda = 1$ unchanged: $\tilde{X}_1 = X_1 = e$. By means of a heuristic threshold value $0 \ll \delta < 1$, which is common for all eigenvectors, we then select those states that exhibit a "stable" sign structure according to:

(S1) Determine $\mathcal{S} = \{s \in \{1, \ldots, n\} : \max_{i=1,\ldots,k} |\tilde{X}_i(s)| > \delta\}$.

Step 2. *Define sign structure classes.* Based on the sign structures of the states in $\mathcal{S}$, we proceed to define k equivalence classes with respect to sign structures. Upon assigning each of the states in $\mathcal{S}$ to one of these k sign structure classes, a surjective map $a : \mathcal{S} \to \{1, \ldots, k\}$ is defined. More details of this assignment process are skipped here, but will be described later. Formally, the second step of the identification algorithm then reads:

(S2) Determine k equivalence classes of sign structures and the associated map a such that $\mathcal{S}$ decomposes into k disjoint subsets $\mathcal{S}_1, \ldots, \mathcal{S}_k$, each of which represents the "core" of the almost invariant aggregates.

Step 3. *Identify piecewise constant level pattern.* We are finally left to assign each of the remaining states $s \in \{1, \ldots, n\} \backslash \mathcal{S}$ to one of the k sign structure classes. Of course, we aim at a complete decomposition of the state space into k aggregates. Rather than using the sign structures of these states, which might be heavily perturbed, we exploit the fact that the k eigenvectors X_i are approximate linear combinations of the k characteristic functions of the aggregates. Since subsets $\mathcal{S}_j$ of each aggregate are already available, we modify the *least-squares fit* (14) such that it is only based on the states in $\mathcal{S}$. For this purpose, we denote by $X_j|_{\mathcal{S}}$ the eigenvectors reduced componentwise to the subset $\mathcal{S}$ of indices. This leads to:

(S3) Evaluate coefficients a_{ji} such that

$$\left\| \chi_{\mathcal{S}_i} - \sum_{j=1}^{k} a_{ji} X_j|_{\mathcal{S}} \right\|_\pi = \text{min!} \quad \text{for } i = 1, \ldots, k.$$

Once the coefficients a_{ji} have been determined over the index set $\mathcal{S}$, we extend the $\chi_{\mathcal{S}_i}$ *to* $\chi_i = \sum_{j=1}^{k} a_{ji} X_j$ over the full index set $1, \ldots, n$. From this we determine the aggregates via

$$A_j = \{s \in \{1, \ldots, n\} : \ \chi_j(s) > \chi_i(s) \text{ for all } i \neq j\}.$$

In case of ambiguity in the above componentwise selection, a state is assigned to an arbitrary aggregate with maximal χ_j (this case has never been observed in any of the numerical experiments performed so far).

Assignment procedures in Step 2. As already indicated, the underlying idea is that only "significantly large" entries in the scaled vectors $\tilde{X}_i$ are permitted to contribute to a sign structure. To this end, we define a sign structure $\sigma(s,\theta)$ for state s with respect to some heuristic *threshold value* θ with $0 < \theta < 1$ by virtue of

$$\sigma(s,\theta) = (\sigma_1, \ldots, \sigma_k) \quad \text{with } \sigma_i = \begin{cases} \operatorname{sign}(\tilde{X}_i(s)) & \text{if } |\tilde{X}_i(s)| > \theta, \\ 0 & \text{otherwise.} \end{cases}$$

Obviously, the threshold value is understood to separate components with a clear sign information from those that might have been perturbed to such an extent that the sign information has been lost. By $\Sigma(\mathscr{S},\theta) = \{\sigma(s,\theta) \mid s \in \mathscr{S}\}$, we denote the set of all sign structures with respect to θ. Two sign structures σ_1 and σ_2 are said to be *equivalent*, written as $\sigma_1 \sim \sigma_2$, iff their pointwise multiplication yields only non-negative entries. This implies that any entry 0—determined via the threshold—may be interpreted arbitrarily either as +1 or −1. Our goal is now to find the smallest threshold $\tilde{\theta}$, for which we can find an unambiguous assignment into exactly k classes, i.e., $\sigma^i \sim \sigma^j$ if $a_{\tilde{\theta}}(\sigma^i) = a_{\tilde{\theta}}(\sigma^j)$ for a surjective map $a_{\tilde{\theta}} : \mathscr{S} \to \{1, \ldots, k\}$.

To find a map a_θ for a given θ, we define a partial ordering $\prec$ on $(\Sigma(\mathscr{S},\theta), \prec)$ by $\sigma^i \prec \sigma^j$ iff $\sigma^i \sim \sigma^j$ and $(\sigma_l^j = 0 \Rightarrow \sigma_l^i = 0)$ for $l = 1, \ldots, k$. Let $\mathscr{S}_{\max}$ be the set of all *maximal* elements given by $(\Sigma(\mathscr{S},\theta), \prec)$. Obviously, if we find a map a_θ on $\Sigma(\mathscr{S}_{\max},\theta)$, we can extend it to $\Sigma(\mathscr{S},\theta)$, because each $\sigma \in (\Sigma(\mathscr{S},\theta) \backslash \Sigma(\mathscr{S}_{\max},\theta))$ can be assigned to the same class as the one of its maximal elements. Hence, by restricting any search to maximal elements only, we expect to drastically reduce the algorithmic complexity.

At this stage, we may directly transform our problem into a *graph coloring* problem, a standard problem in graph theory—see [13]. Let $\mathscr{G}(\mathscr{S}_{\max}, E)$ be the graph, where each maximal element is represented by a vertex and $(\sigma^i, \sigma^j) \in E \Leftrightarrow \sigma^i \not\sim \sigma^j$, i.e., maximal elements which are not equivalent are connected by edges. The idea behind this definition of $\mathscr{G}$ is that a k-coloring decomposes $\mathscr{S}_{\max}$ into k classes, so that the elements of each class are mutually equivalent. In our algorithm, we implemented a sequential coloring heuristics with recursive smallest last ordering as described in detail, e.g., in [13]. In this way, we exploit the fact that the chromatic number $\chi_{\mathscr{G}}$ monotonically decreases from $\chi_{\mathscr{G}} = l$ with $l \geqslant k$ for $\theta = 0$ to $\chi_{\mathscr{G}} = 1$ for $\theta = 1$.

We thus arrive at the following procedure to compute k classes $\sigma_1^*, \ldots, \sigma_k^*$ of sign structures:

set $\theta^- = 0$ and $\theta^+ = 1$ to perform a bisection
set m as the number of bisection steps
for $j = 1$ to m **do**
    set $\tilde{\theta} = (\theta^- + \theta^+)/2$
    determine $\Sigma(\mathscr{S},\tilde{\theta})$, $\Sigma(\mathscr{S}_{\max},\tilde{\theta})$ and $\mathscr{G}(\mathscr{S}_{\max}, E)$
    compute a coloring of $\mathscr{G}$
    set $\tilde{\chi}_{\mathscr{G}}$ the number of colors, which should be equal or close to $\chi_{\mathscr{G}}$

if $\tilde{\chi}_{\mathcal{G}} \geqslant k$ **then**

$\theta^+ = \tilde{\theta}$

else

$\theta^- = \tilde{\theta}$

end if

end for

if $\tilde{\chi}_{\mathcal{G}} = k$ for $\theta = \theta^+$ **then**

determine the k color sets $\tilde{\mathcal{S}}_1, \ldots, \tilde{\mathcal{S}}_k$

set $\sigma_i^* = \text{sign}\left(\sum_{\sigma \in \tilde{\mathcal{S}}_i} \sigma\right)$

else

go back to (S1) and choose another value for δ

(this case is rare and never occurred in our examples).

end if

Having terminated with k sign structures $\sigma_1^*, \ldots, \sigma_k^*$, we still have to compute the associated decomposition of $\mathcal{S}$ yielding the core sets $\mathcal{S}_1, \ldots, \mathcal{S}_k$. This is done as follows: We start with $\mathcal{S}_i = \emptyset$ for all $i = 1, \ldots, k$. Then, successively for all states s_j from $\mathcal{S}$: Set $\theta = 0$, and increase θ until there is an $r \in \{1, \ldots, k\}$ such that $\sigma(s_j, \theta) \sim \sigma_r^*$. If r is unique, assign s_j to $\mathcal{S}_r$, i.e., set $\mathcal{S}_r = \mathcal{S}_r \cup \{s_j\}$, otherwise we do *not* assign the state s_j to any of the $\mathcal{S}_i$. If any of the $\mathcal{S}_i$ remain empty, then the whole procedure has failed and must be restarted with smaller δ in step (S1).

Remark. We managed to transform our problem into the NP-*complete* problem of graph coloring. Hence, *heuristics* are anyway justified to play a crucial role in its computational solution. Under the additional constraint of a perturbed piecewise constant level pattern in the eigenvectors, however, the space of permitted colorings of the corresponding graph $\mathcal{G}(\mathcal{S}_{\max}, \tilde{\theta})$ is restricted—making our problem less complex than a general unconstrained graph coloring problem.

5. Numerical experiments

We now want to illustrate the performance of our suggested identification algorithm by two examples, one rather simple artificial example and one example from molecular dynamics out of the problem class that has motivated this investigation.

5.1. Illustrative artificial example

This simple model problem is mainly presented to illustrate the perturbation theory as given in Theorem 3.1. We construct a reversible primitive stochastic matrix P

with $k = 3$ blocks as follows: we first generate a symmetric block diagonal matrix D with three blocks and a strictly positive symmetric perturbation matrix E, both with equidistributed random entries. For $0 < \mu < 1$, we define the symmetric matrix

$$P_{\text{sym}} = (1 - \mu)D + \mu E. \tag{16}$$

By normalizing $P_{\text{sym}} = ((p_{\text{sym}})_{ij})$ such that $\sum_{i,j=1}^{n}(p_{\text{sym}})_{ij} = 1$, we obtain a *reversible row stochastic* matrix $P = (p_{ij}) = ((p_{\text{sym}})_{ij}/\pi_i)$ wherein the stationary distribution $\pi = (\pi_i)$ is defined via

$$\pi_i = \sum_{j=1}^{n}(p_{\text{sym}})_{ij}.$$

If at least one of the diagonal entries p_{ii} is different from zero (which is easy to check), then P is also *primitive*—see e.g. [4]. Fig. 2 shows an associated eigenvector basis $\{X_1, X_2, X_3\}$ of such a matrix that has been constructed as described with $\mu = 0.3$.

Computation of eigenbasis. The Perron cluster of eigenvalues came out as $(\lambda_1, \lambda_2, \lambda_3) = (1, 0.75, 0.52)$. The associated eigenvectors X_1, X_2, X_3 are given in Fig. 2. Compared with the related uncoupled case presented in Fig. 1, the sign structure is still visible in the perturbed eigenspace basis, though an erratic sign structure occurs close to the zero unperturbed level of X_3. As can be seen, there is no difficulty to identify the three almost invariant aggregates "by eye".

Almost invariant aggregates. Next, the coefficient matrix $\mathcal{A} = (a_{ji})$ of dimension $k \times k$ has been computed on the basis of the least-squares fit (14). Fig. 3 compares the linear combination of the eigenvectors $\sum_j a_{ji} X_j$ with the constant level characteristic functions χ_{A_i} that are the object of interest. Despite the relatively wide spreading of the Perron cluster, the approximation of the χ_{A_i} is indeed intriguing.

Coupling matrix. In the next step, we compute the coupling matrix W according to Definition 2.4 for the given decomposition into the three almost invariant aggregates A_1, A_2, A_3. Here we obtain the diagonally dominant matrix

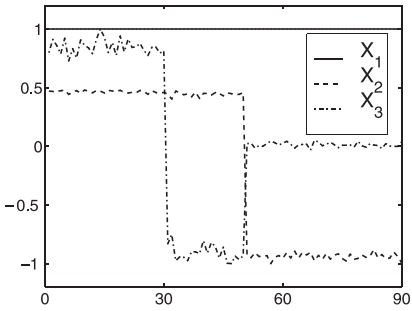

Fig. 2. Eigenspace basis X_1, X_2, X_3 corresponding to Perron cluster $\lambda = 1, 0.75, 0.52$ of the transition matrix associated with $k = 3$ nearly uncoupled Markov chains. Observe the nearly constant level pattern on each of the aggregates A_1, A_2 and A_3—to be compared with Fig. 1 for the uncoupled case.

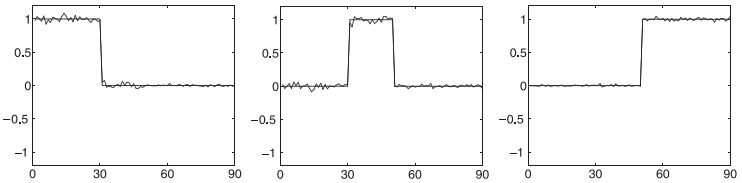

Fig. 3. Illustration of approximate characteristic functions for almost invariant aggregates of the artificial example from Fig. 2. Each of the figures shows one of the characteristic functions χ_{A_i} and its approximation $\sum_j a_{ji} X_j$ (notation see text).

$$W = \begin{pmatrix} 0.7271 & 0.1943 & 0.0786 \\ 0.2039 & 0.7138 & 0.0823 \\ 0.0829 & 0.0827 & 0.8343 \end{pmatrix}.$$

According to (12) this yields the perturbation parameter $\epsilon_* = 0.2862$.

Error indicator. Recall the definition of the error indicator as given in (15). With the Perron cluster Λ, the coefficient matrix $\mathscr{A}$, and the coupling matrix W already computed, we are able to evaluate this matrix as

$$\mathrm{err} = \begin{pmatrix} 0.0198 & 0.0222 & -0.0421 \\ 0.0235 & 0.0202 & -0.0437 \\ 0.0223 & 0.0212 & -0.4340 \end{pmatrix}.$$

The information in terms of the two matrices W and err substantiates the following observations: (a) the influence of the weak modes on the coupling of the aggregates may be neglected in this example, and (b) the probabilities to stay within the aggregates is not really close to one, which seems to be a consequence of the spreading of the Perron cluster.

5.2. *Metastable conformations of n-pentane*

Our identification algorithm has already been successfully applied to (moderate size) biomolecules (see [2,14]). For the purpose of illustration, we select the quite small well understood *n*-pentane molecule CH_3–$(CH_2)_3$–CH_3—see Fig. 4(a). The

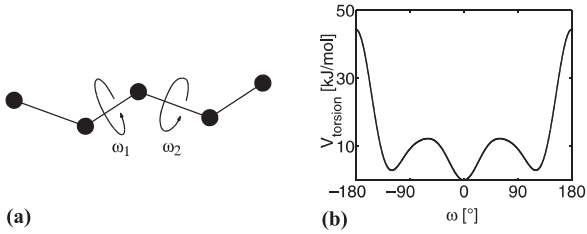

Fig. 4. (a) United atom model of *n*-pentane with the two dihedral angles $\omega = (\omega_1, \omega_2)$. (b) Dihedral angle potential due to Ryckaert and Bellemans [15]. Central minimum: main angular orientation (*trans*), left and right minimum: $-$*gauche* and $+$*gauche* orientations.

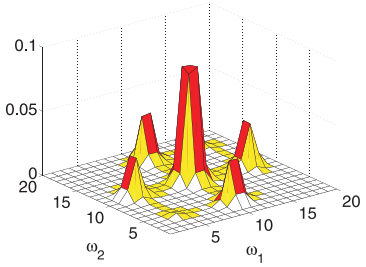

Fig. 5. Stationary distribution π in dihedral angle plane (ω_1, ω_2).

most flexible part of the molecule is characterized by the so-called dihedral angles ω_1, ω_2—see Fig. 4(b), for the two potentials with three minima each. Within chemistry, the orientations (*trans* or *gauche*) of these dihedral angles are known to give rise to different "conformations" of the molecule.

By means of a *hybrid Monte Carlo method* (compare [2]) a primitive and reversible stochastic 400×400 matrix P has been generated. The left eigenvector π is given as a spatial projection of the well-known Boltzmann distribution—see Fig. 5.

Perron cluster. The first 10 eigenvalues of P, ordered with respect to absolute value, are:

k	1	2	3	4	5	6	7	8	9	10
λ_k	1	0.986	0.984	0.982	0.975	0.941	0.938	0.599	0.590	−0.562

The first nine ones are seen to be positive. From the 10th one onwards negative eigenvalues appear. Obviously, the largest gaps arise between λ_5 and λ_6, and, even more significantly, between λ_7 and λ_8. Therefore we present the results of the identification algorithm both for $k = 5$ and for $k = 7$.

Corresponding eigenbasis. The right eigenvectors corresponding to $\lambda_1 = 1$ (a) and $\lambda_2 = 0.986$ (b) are illustrated in Fig. 6. Of course, for $\lambda_1 = 1$, we obtain $e = (1, \ldots, 1)^{\mathrm{T}}$, which in grid representation is just a flat plateau (ignoring zeroes for cut-off states). For λ_2, the right eigenvector contains more information. Just as in

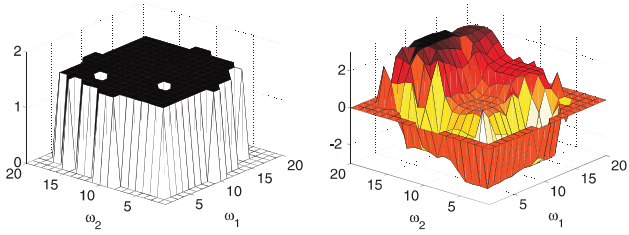

Fig. 6. (a) Right eigenvector for eigenvalue $\lambda_1 = 1$ in an (ω_1, ω_2)-plane. Zero entries are cut-off states (probability for the dynamical system to be within these states neglected). (b) Right eigenvector for eigenvalue $\lambda_2 = 0.9859$. Observe nearly constant levels.

our model example (see Fig. 2), we can distinguish between different plateau levels, which seem to indicate different almost invariant aggregates. Fig. 7 represents the first seven eigenvectors split into their positive and negative parts (as described in Section 4). The *right* eigenvectors show the expected almost constant level structure, which allows the state space to be decomposed using the algorithm explained in Section 4. In contrast to this, the *left* eigenvectors have distinct maxima only at the center of each constant level.

Almost invariant aggregates ($k = 5$). Our identification algorithm ended up with the almost invariant aggregates $A_1, \ldots, A_5$ as illustrated in Fig. 8. The *transition probabilities* $w(A_i, A_j)$ between these aggregates are arranged in the following *coupling matrix*:

$$W = \begin{pmatrix} 0.9783 & 0.0006 & 0.0162 & 0.0038 & 0.0011 \\ 0.0006 & 0.9774 & 0.0145 & 0.0007 & 0.0070 \\ 0.0044 & 0.0042 & 0.9823 & 0.0042 & 0.0049 \\ 0.0040 & 0.0008 & 0.0162 & 0.9786 & 0.0004 \\ 0.0010 & 0.0066 & 0.0162 & 0.0004 & 0.9759 \end{pmatrix},$$

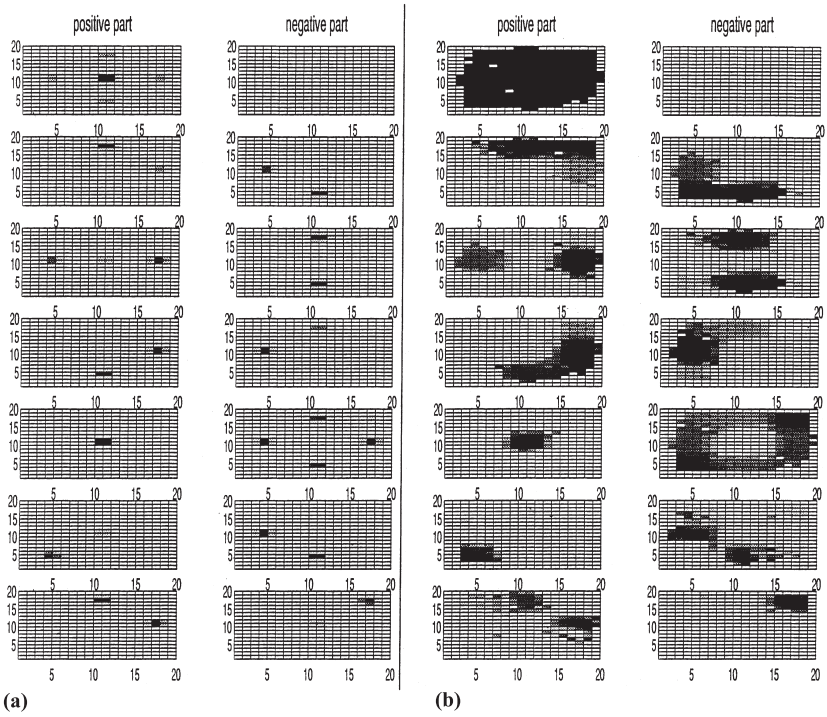

Fig. 7. $k = 7$: *Left* (a) and *right* eigenvectors (b). Grey scaling with respect to maximum norm. First row right: cf. Fig. 6(a). Second row right: compare Fig. 6(b).

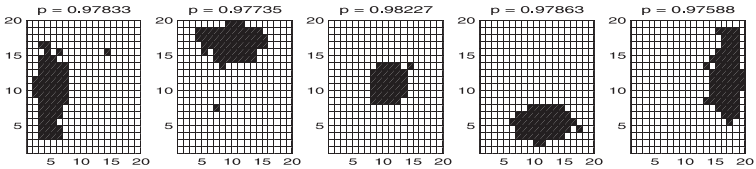

Fig. 8. Almost invariant aggregates for $k = 5$. The values p denote the probabilities to stay within these aggregates during the discrete time step $\tau = 160$ fs.

where the ordering of the aggregates corresponds to Fig. 8. Recall that the diagonal entries in W show the high probabilities for the molecular system to stay within A_i, once it is in A_i. According to (12) this coupling matrix yields the perturbation parameter $\epsilon_* = 0.0241$.

The corresponding *error indicator* is

$$\mathrm{err} = \begin{pmatrix} -0.0071 & -0.0006 & 0.0071 & 0.0015 & -0.0007 \\ -0.0010 & -0.0098 & 0.0065 & -0.0005 & 0.0046 \\ -0.0007 & 0.0001 & -0.0016 & 0.0011 & 0.0011 \\ 0.0008 & -0.0009 & 0.0081 & -0.0071 & -0.0003 \\ -0.0016 & 0.0037 & 0.0066 & -0.0003 & -0.0091 \end{pmatrix}.$$

The fact that all its entries are small indicates that the identification process is reliable.

Almost invariant aggregates ($k = 7$). The seven aggregates shown in Fig. 9 were identified. Observe that the eigenvectors corresponding to λ_6 and λ_7 (see Fig. 7) contain the additional information about the separation of the so-called +gauche/+gauche- and the −gauche/−gauche-conformation (see caption of Fig. 4 for terminology). Therefore, we obtain a more detailed partitioning of the state space, even though the probabilities to stay within the additional conformations are lower. If we again use (12), we now obtain the perturbation parameter $\epsilon_* = 0.0823$, slightly larger than for $k = 5$; such an increase is expected, since splitting almost invariant aggregates into parts can shift the minimum in formula (12) only to this side.

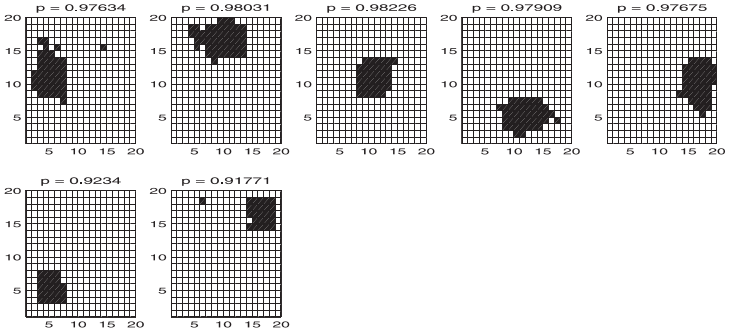

Fig. 9. Almost invariant aggregates for $k = 7$. Observe the splitting of aggregates compared with Fig. 8.

Summarizing, the example clearly demonstrates that the algorithm can produce satisfactory results, even if almost invariant aggregates exhibit substructures corresponding to smaller eigenvalues in the Perron cluster. Both results, for $k = 5$ and for $k = 7$, are in good agreement with chemically observed conformations. What is most important, however: our new identification algorithm has automatically detected the known chemical conformations without explicit a priori use of chemical insight.

Acknowledgements

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