From Metastable to Coherent Sets – time-discretization schemes

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Given a time-dependent stochastic process with trajectories $x(t)$ in a space Ω, there may be sets such that the corresponding trajectories only very rarely cross the boundaries of these sets. We can analyze such a process in terms of metastability or coherence. *Metastable sets* M are defined in space $M \subset \Omega$, *coherent sets* $M(t) \subset \Omega$ are defined in space and time. Hence, if we extend the space Ω by the time-variable t, coherent sets are metastable sets in $\Omega \times [0, \infty)$. This relation can be exploited, because there already exist spectral algorithms for the identification of metastable sets. In this article we show that these well-established spectral algorithms (like PCCA+) also identify coherent sets of non-autonomous dynamical systems. For the identification of coherent sets, one has to compute a discretization (a matrix T) of the transfer operator of the process using a space-time-discretization scheme. The article gives an overview about different time-discretization schemes and shows their applicability in two different fields of application.

I. INTRODUCTION TO THEORY

Metastability and coherence are related concepts in mathematics. Algorithmically, the analysis of metastable or coherent sets is achieved by spectral decomposition of a transfer operator [29]. In the following, it will be explained how these transfer operators are constructed.

A. Metastability

Metastable sets are understood in the following sense [3], where the definition was chosen such that it is straightforward to generalize to coherent sets.

Definition: *Given a stochastic dynamical system with trajectories $x(t) \in \Omega$ in a space Ω, its invariant measure μ, and a time scale $\eta > 0$, then a* metastable set *is a subset $M \subset \Omega$, such that if and only if a trajectory with μ-distributed initial condition starts in M it will stay in M (i.e. $x(t) \in M$) with a high probability for all $0 \leq t < \eta$.*

Note that this definition also includes deterministic systems. Many applications exist in which this type of metastability is used [3, 17]. One important class of applications is molecular simulation [34]. The binding process of a ligand to a receptor, or the folding process of proteins consist of a cascade of rare jumps between metastable sets in conformational space [5]. These sets are metastable on time scales much larger than the time stepping (usually 1fs) of molecular simulations, which illustrates the choice of η. In the past decades, algorithmic tools have been developed to identify these metastable sets and the expected time scales of the rare jumps between them [4, 27]. These algorithms mainly aim at completely or partially decomposing Ω into subsets which are all metastable.

For the analysis of metastabilities, usually a transfer operator based approach is used [29]. More precisely, a transition kernel $p^\tau(x, A)$ is derived that provides the conditional probability to be in a measurable set $A \subset \Omega$ from a starting point $x \in \Omega$ after a time interval of length τ. This transition kernel is reformulated in terms of a transfer operator $\mathcal{P}^\tau$, which is uniquely given by the characterization [21, 25]

$$\int_\Omega p^\tau(x, A)\, f(x)\, \mu(dx) = \int_A \big(\mathcal{P}^\tau f\big)(x)\, \mu(dx), \tag{1}$$

that should hold for all measurable sets A and all $f \in L^1(\mu)$. In this equation it is advantageous to let μ be the stationary measure of the process. If it is a reversible process, then $\mathcal{P}^\tau$ is μ-self adjoint. In general, the choice of μ is not fixed, but it is only necessary that p is μ-compatible[25]. In the following, it is only important that the identification of metastabilities is solved by constructing a transfer operator $\mathcal{P}^\tau$. The spectral properties of $\mathcal{P}^\tau$ characterize the metastabilities and the implied time scales of the rare jumps.

In principle, one can discriminate between two different ways to identify the transfer operator. The **trajectory-based approach** is directly connected to the definition of a metastable set. The trajectories can originate from the numerical solution of (stochastic) differential equations [18], or they can come from the analysis of time-series data [29]. The time-series data can be used directly as a trajectory in Ω, or, alternatively, it could be a series of images, in which certain objects move [37]. The trajectories are then indirectly provided by a tracking analysis of those objects. In the trajectory-based approach the trajectories (assuming an autonomous system) are usually used in order to derive the transition pattern of a Markov process in Ω from the data, and a discretized transfer operator is constructed, e.g., by Ulam's method [32].

For later use, let us remark that for non-autonomous systems (or non-homogeneous, in the stochastic language) the transition kernel depends on the starting time t as well, i.e., $p^\tau(t, x, A)$, which leads to a time-dependent transfer operator $\mathcal{P}^\tau(t)$ by solving the above integral equation for every $t \in [0, \infty)$. The analysis of non-autonomous metastable molecular systems via transfer operators only started recently [22, 30], while for atmospheric and fluid dynamic problems they have been developed earlier [10, 12, 13].

In the **ensemble-based approach** the underlying (possibly stochastic) dynamics is not known or used explicitly to construct the transfer operator. This approach is often connected to chemical or physical measurements of densities (or distribution of states). Instead of observing single trajectories in a finite dimensional space Ω, one observes how a density function $\pi(t)(\cdot) : \Omega \to \mathbf{R}$ changes in time (electron density, concentrations, cloud intensities, population density, etc.). The deterministic time-dependent evolution $\pi(t)$ of densities can be assumed to be the solution of an initial value problem

$$\frac{d}{dt}\pi(t) = \mathcal{Q}\pi(t) \quad \text{or} \quad \pi(t+1) = \mathcal{Q}\pi(t)\,,$$

depending on whether we consider continuous or discrete time systems. To build a bridge to the trajectory-based point of view: The evolution of densities is physically understood as a result of infinitely many "transporting" stochastic

trajectories. One example for such a deterministic initial value problem is the Fokker–Planck equation, where $\mathcal{Q}$ is the Fokker–Planck operator. The trajectory-based point of view for this equation is particles moving with Brownian motion guided by a potential energy landscape.

The solution of an initial value problem (in the autonomous case) can be formulated in terms of a propagator $\pi(t+\tau) = \widetilde{\mathcal{P}}^\tau \pi(t)$, providing the density function $\pi(t+\tau)$ at time $t+\tau$, if the initial density function $\pi(t)$ is given. It can be shown that this propagator $\widetilde{\mathcal{P}}^\tau$ is similar to the transfer operator $\mathcal{P}^\tau$ defined above. $\mathcal{P}^\tau$ and $\widetilde{\mathcal{P}}^\tau$ are the Perron–Frobenius operators, with regard to different base measures (μ and Lebesgue). Thus, the same kind of algorithms are used for the ensemble-based approach: A spectral analysis of $\mathcal{P}^\tau$ provides the desired information about metastabilities.

However, if the ensemble-based process is non-autonomous, then the corresponding propagator $\pi(t+\tau) = \widetilde{\mathcal{P}}^\tau(t)\pi(t)$ is time-dependent, i.e., $\widetilde{\mathcal{P}}^\tau(t)$ depends on τ and t, just as the adjoint transfer operator. In this case, the Fokker–Planck operator $\mathcal{Q} = \mathcal{Q}(t)$ would be time-dependent too.

All these approaches have been established during the past two decades. The question how to interpret the eigenfunctions and eigenvalues of $\mathcal{P}^\tau$ have been answered early. The question how to efficiently find a discretized version of $\mathcal{P}^\tau$ for spectral analysis has been answered partially, and is still subject of intense research. Also the question of how to deal with non-autonomous propagators $\widetilde{\mathcal{P}}^\tau(t)$ has been discussed already.

B. PCCA+

The identification of metastable sets from the (discretized) transfer operator can be achieved with the PCCA+ algorithm [7]. If one tries to project a Markov process from a high-dimensional space Ω to a Markov chain on a finite number of metastable sets, then only an invariant subspace projection preserves time-scales and the Markovian nature of the process[23]. Thus, in the PCCA+ a basis X of a ℓ-dimensional invariant subspace of $\mathcal{P}^\tau$ is taken and a basis transform $\chi = XA$, $A \in \mathbf{R}^{\ell\times\ell}$ is performed, such that the new basis functions $\chi_1, \ldots, \chi_\ell : \Omega \to [0,1]$ can be regarded as membership functions of metastable sets (although "fuzzy sets" would be more precise) of the process. The invariant subspaces X are usually spanned by eigenfunctions of $\mathcal{P}^\tau$ if it has according spectral properties. For this reason, eigenspaces and eigenvalues play an important role in metastability analysis. For identifying the invariant subspaces of general transfer operators $\mathcal{P}^\tau$, the Schur decomposition can be used, see Sec. II A.

C. Coherent sets

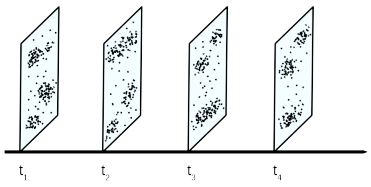

FIG. 1. Time slices of particles moving due to a Markov process. Note that our method of identifying coherent sets also allows for a transition between separated and connected sets $M(t)$ along time. For an example of unification, see bottom from t_1 to t_4. Top shows an example for separation.

Next, the theory is extended from metastable sets to coherent sets. The definition of coherent sets is chosen to be similar to the definition of metastable sets. We call a time-parametrized family of densities μ_t *equivariant*, iff $\widetilde{\mathcal{P}}^{(t,\tau)}\mu_t = \mu_{t+\tau}$ for all t and $\tau > 0$.

Definition: *Given a stochastic dynamical system with trajectories $x(t) \in \Omega$, an equivariant family of distributions μ_t, and a time scale $\eta > 0$, then a* coherent set *is a time-dependent subset $M(t) \subset \Omega$, such that if and only if $x(s)$ is μ_s-distributed and $x(s) \in M(s)$, then $x(t) \in M(t)$ with a high probability for all $0 \le s < t < \eta$.*

We remark that this definition also includes coherent sets which occur at some time $t > 0$ and/or vanish at some time $t < \eta$, if $M(t) = \emptyset$ is allowed. Note that this is conventionally not the case, as it is assumed that all the $M(t)$ have the same "size" measured by the distributions μ_t [12, 13, 22]; i.e., $\int_{M(t)} \mu_t = \text{const}$. Also, coherent sets are not

necessarily connected in state, they might split or merge as time progresses; see also Fig. 1. Note that, by definition, metastable sets are also coherent sets but without any time dependence, i.e., $M(t) \equiv M(0)$.

The opposite view has been established in [9]: coherent sets are metastable sets in "space-time". Simply speaking, metastable and coherent sets define boundaries in space or space-time, respectively, which are rarely crossed by trajectories. For analyzing coherent sets one has to extend the space Ω to space-time $\Omega \times [0, \infty)$. Based on this observation, it is straightforward to construct the transfer operator in space-time for the mentioned spectral-analysis based algorithms, which would then solve the coherent set problem.

If $\mathcal{P}^\tau(t)$ is the non-autonomous transfer operator acting on functions $f : \Omega \to \mathbf{R}$ derived from either trajectories or ensembles, then one can define an autonomous transfer operator $\mathcal{T}^\tau$ which acts on functions $\hat{f} : \Omega \times [0, \infty) \to \mathbf{R}$ via

$$\big(\mathcal{T}^\tau \hat{f}\big)(x,t) := \Big(\big(\mathcal{P}^\tau(t) f(t)\big)(x), t + \tau\Big), \tag{2}$$

where $f(t)(x) = \hat{f}(x,t)$. The family $\{\mathcal{T}^\tau\}_{\tau \geq 0}$ is called the *evolution semigroup* [6], and a spectral analysis of the operator $\mathcal{T}^\tau$ in $\Omega \times [0, \infty)$ provides the results of a coherent set analysis of $\mathcal{P}^\tau(t)$ in Ω, cf. [9] for a precise connection in the case of time-periodic non-stationarity, and further references.

Two major problems remain:

1. The transfer operator $\mathcal{P}^\tau$ which is usually used for spectral analysis may have advantageous spectral properties. Time-reversible processes lead to self-adjoint transfer operators and, thus, to real eigenvalues and real eigenfunctions. The transfer operator $\mathcal{T}^\tau$ is non-reversible by construction, thus its sepctrum is not real. The interpretation of complex eigenvalues in terms of coherence is possible for time-periodic systems [9], but has not been established yet in the general case.

2. The transfer operator $\mathcal{T}^\tau$ needs to be discretized for the numerical linear algebra algorithms for spectral analysis. In space-time domain $\Omega \times [0, \infty)$ one has to restrict the time to the finite time-interval $[0, \eta]$. This "lifted system" has sources ($t = 0$) and sinks ($t = \eta$) and a discretization at these "singularities" may be difficult.

This article proposes some solutions to these two problems.

D. Time-Discrete or finite Markov processes

In the above definitions it is always assumed to have trajectories $x(t)$. This does not imply that $x(t)$ is a continuous trajectory in time. There are two ways to include time-discrete Markov processes into this framework:

- If the process is a Markov chain, then the time interval can be assumed to be constant. In this case the time-discretization in the next section is always performed with a constant interval τ.
- A time-discrete process can also be regarded as an non-autonomous process, where $\mathcal{P}^\tau(t) = \mathcal{I}$ is the identity operator, if and only if there is no time-step of the Markov process within the interval $[t, t+\tau]$. Otherwise, $\mathcal{P}^\tau(t)$ is the transfer operator of that transition.

Furthermore, the set Ω can be a finite set. In that case $\mathcal{P}^\tau(t)$ is a family of transition matrices.

II. METHODS

The coherent set analysis of *autonomous* transfer operators does not necessarily need the definition of $\mathcal{T}^\tau$. If the transfer operator $\mathcal{P}^\tau$ is *autonomous and reversible*, then coherent sets are identical to metastable sets. This is due to the fact that coherent sets can be extracted from singular vectors of the transfer operator [13], and metastable sets from eigenvectors. For self-adjoint operators, these objects are identical. The corresponding analysis is simple to perform numerically. $\mathcal{P}^\tau$ usually has well-conditioned real eigenspaces corresponding to clustered real eigenvalues. Only the cases that the process is non-reversible or that it is non-autonomous are challenging. However, the case of an *autonomous, non-reversible* system can in principle be solved easily, too. In this case, one replaces the analysis of eigenfunctions by the analysis of invariant subspaces of the operator $\mathcal{P}^\tau$. This type of analysis is explained in Sec. II A, it is also discussed in [19].

The only remaining problem is to study *non-autonomous* processes in terms of coherent sets. In this case a metastability analysis of $\mathcal{T}^\tau$ in (2) has to be done. For spectral analysis of $\mathcal{T}^\tau$, one needs to discretize the operator. Let us first assume that we have already decomposed the space Ω into n subsets and apply Ulam's method for the

space-discretization of $\mathcal{T}^\tau$. In Sec. II F we will discuss alternatives to this assumption. After space-discretization using n subsets, the transfer operator turns into a family of matrices $T^\tau(t) \in \mathbf{R}^{n\times n}$ which is still time-dependent. Note that at this point $T^\tau(t)$ is just the discretization of $\mathcal{P}^\tau(t)$. In order to construct one (large) matrix $T \in \mathrm{R}^{nm\times nm}$ out of this family one has to find a suitable time-discretization into m time steps. This full space-time-discretization will provide a stochastic matrix T, which gives rise to a time-homogeneous "space-time" discrete Markov chain. The analysis of autonomous, non-reversible transition matrices is explained next, before we turn to the question how to assemble the $T^\tau(t)$ into one transition matrix T that can be then subject to metastability analysis.

A. Schur Decomposition

An autonomous, non-reversible Markov process can be analyzed in terms of metastable sets or dominant cycles (a sequence of transient states). After space-discretization the Markov process turns into a Markov chain with a transition matrix T. Computing eigenvalues of a non-reversible transition matrix T can be numerical demanding, i.e., ill-conditioned. The interpretation of complex eigenvalues or eigenvectors can be ambiguous in the PCCA+ framework. In literature [8, 35], it was already proposed to replace an eigenvalue analysis of T by a real Schur decomposition of this matrix, which generally provides the invariant subspaces of T. The algorithm PCCA+ for the identification of metastable sets is usually based on eigenvectors as input data, but it also works with real Schur vectors as input data without changing any algorithmic details.

B. Push-forward time-discretization

The last question to be answered is how to discretize time. The problem of an infinite time interval $[0,\infty)$ is avoided by taking the definition of a coherent set that includes a final time η of consideration. By taking $\eta < \infty$ we consider so-called *finite-time coherent sets* here [13]. There are concepts of coherence where time can run to infinity, e.g., in the periodic setting [9], or as considered in the framework of *multiplicative ergodic theory* [14]. In this latter case, however, one needs knowledge of the system for all times, and this is especially in data-driven applications not the case.

We now decompose the time interval $[0,\eta]$ into m small intervals of length τ. Thus, the space $\Omega\times[0,\eta]$ is decomposed into $n\cdot m$ sets. A space-time discretized version of $\mathcal{T}^\tau$ would, thus, be a matrix $T_{pf} \in \mathbf{R}^{nm\times nm}$, which consists of m^2 block matrices of size $n\times n$. For the case of $m=4$ the matrix T_{pf} consists of 16 block matrices:

$$T_{pf} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ T^\tau(0) & 0 & 0 & 0 \\ 0 & T^\tau(\tau) & 0 & 0 \\ 0 & 0 & T^\tau(2\tau) & 0 \end{pmatrix}. \tag{3}$$

The problem of this push-forward discretization is that it is an open system: everything from the k-th time interval is pushed into the $(k+1)$-st time interval, which results eventually pushing everything from the m-th time interval "out of the system". Thus, there is no metastability in this system at all, as it is also nicely reflected by the spectrum: T_{pf} is a nilpotent matrix, thus has no eigenvalues close to one, because all of its eigenvalues are zero. This is the reason why a push-forward time-discretization will not work.

C. Time-decoupled analysis

Instead of decomposing the time interval $[0,\eta]$ and filling the off-diagonal elements of T_{pf} like in (3), one can also assume that the transition matrices $T^\tau(0),\ldots,T^\tau(3\tau)$ are representative for the whole time-intervals and insert them onto the diagonal of a matrix T_{td}. For the case $m=4$:

$$T_{td} = \begin{pmatrix} T^\tau(0) & 0 & 0 & 0 \\ 0 & T^\tau(\tau) & 0 & 0 \\ 0 & 0 & T^\tau(2\tau) & 0 \\ 0 & 0 & 0 & T^\tau(3\tau) \end{pmatrix}. \tag{4}$$

In this approach it turns out that the coherent set analysis of a non-autonomous system is replaced by m metastable set analyses of autonomous Markov chains like shown in Sec. II A. However, the continuity of the trajectories $x(t)$ is discarded in this approach. The intervals are not "connected", which may lead to an assignment problem of the

coherent sets $M(t) \to M(t+\tau)$. This analysis will hence only work in a "quasi-stationary" case, i.e., when $T^\tau(k\tau)$ barely changes for $k = 0, \ldots, m-1$.

D. Periodic processes

There is a simple way to use the discretization in (3), filling the last row of block matrices while still preserving the connection between the time intervals. Whenever the autonomous process has a "periodic outer stimulus", i.e., if the time discretization of $\mathcal{T}^\tau$ periodically leads to the same discretized objects, they can be arranged in the following way (for $m = 4$ and $T^\tau(4\tau) = T^\tau(0)$):

$$T_p = \begin{pmatrix} 0 & 0 & 0 & T^\tau(3\tau) \\ T^\tau(0) & 0 & 0 & 0 \\ 0 & T^\tau(\tau) & 0 & 0 \\ 0 & 0 & T^\tau(2\tau) & 0 \end{pmatrix}. \tag{5}$$

T_p is non-reversible, but its dominant real eigenvalues and corresponding eigenfunctions yield time-periodic coherent families $M(t) = M(t+\eta)$, whereas eigenvectors for complex eigenvalues yield quasi-periodic (also called multi-periodic) coherent sets $M(t) := \hat{M}(t,t) = \hat{M}(t+\eta,t) = \hat{M}(t,t+\Theta)$, whith some set-valued function $\hat{M}$ depending on two variables, and $\Theta > 0$ that can be obtained from the imaginary part of the eigenvalue [9, Remark 24].

E. Forward-backward analysis

If the system is not genuinely time-periodic with period η, it is often meaningless to introdice an artificial periodicity in time, since $M(0)$ and $M(\eta)$ might be far apart. The "finite time coherent pairs" setting, introduced by Froyland et al [13] deals with this case through singular value analysis (opposed to eigenvalue analysis) of $T^\eta(0)$. They observe, that their method actually does an eigenvalue analysis of the *forward-backward* transfer operator $T^{-\eta}(\eta)T^\eta(0)$, where $T^{-\eta}(\eta)$ is the (discretized) transfer operator of the time-reversed process $x^-(t) := x(\eta - t)$. The reason for the connection is that $T^{-\eta}(\eta)$ is the adjoint of $T^\eta(0)$, and thus singular values and -vectors of $T^\eta(0)$ are exactly eigenvalues and -vectors of $T^{-\eta}(\eta)T^\eta(0)$. Thus, a set $M(0)$ will stay coherent for time η (meaning, there will be sets $M(t)$, $0 \le t \le \eta$ with which it satisfies the definition of coherence), if and only if it is metastable under the discrete-time forward-backward process having the transition matrix $T^{-\eta}(\eta)T^\eta(0)$, cf [22]. Note that in general the transfer operator of the time-reversed process is *not* the inverse of the transfer operator of the original process, i.e., $T^{-\eta}(\eta)T^\eta(0) \neq I$, where I is the identity matrix. Equality holds only if the process is genuinely deterministic, and in that case the concept of finite time coherence is made sensible by including a vanishing amount of diffusion [10, 11].

The forward-backward process is by construction reversible, and can be seen as a periodic process with the period consisting of two time intervals: the forward process runs on the first one, and the backward process on the second one. Invoking (5), we can consider

$$T_{cp} = \begin{pmatrix} 0 & T^{-\eta}(\eta) \\ T^\eta(0) & 0 \end{pmatrix}, \tag{6}$$

which will give us coherent pairs $M(0), M(\eta)$, since the first row corresponds to time 0, and the second to time η, where the backward process starts. It is a straightforward calculation to see that every eigenvector $(u_0^T, u_\eta^T)^T$ of T_{cp}, where $u_0, u_\eta \in \mathbf{R}^n$, satisfies that u_η is an eigenvector of $T^{-\eta}(\eta)T^\eta(0)$, and the corresponding eigenvalues are the same.

As we would like to formulate the coherence problem as a metastability problem in space-time, we need to include all time slices at once. This can be done by arranging the time-reversed transition matrices on the lower sub-diagonal of T, which can be regarded as a time-expanded variant of (6). For $m = 4$, it reads:

$$T_{rev} = \begin{pmatrix} 0 & T^{-\tau}(\tau) & 0 & 0 \\ \frac{1}{2}T^\tau(0) & 0 & \frac{1}{2}T^{-\tau}(2\tau) & 0 \\ 0 & \frac{1}{2}T^\tau(\tau) & 0 & \frac{1}{2}T^{-\tau}(3\tau) \\ 0 & 0 & T^\tau(2\tau) & 0 \end{pmatrix}, \tag{7}$$

where $\tau = \frac{\eta}{m-1}$. $T_{rev} \in \mathbf{R}^{mn \times mn}$ is a self-adjoint matrix and has real eigenvalues and eigenvectors which can be used for PCCA+. This type of discretization emphasizes the "if-and-only-if"-character of the coherent set definition by regarding the forward *and* backward processes [22].

It is interesting to investigate the connection between the eigenvalue problems for (7) and (6). We considered the case $m = 2$ in (6), so let $m = 3$, and assume that T_{rev} has an eigenvector $(u_0^T, u_\tau^T, u_{2\tau}^T)^T$, where $u_0, u_\tau, u_{2\tau} \in \mathbf{R}^n$. Some algebraic manipulation (that we omit) gives that u_τ is an eigenvector of

$$\frac{1}{2}\left(T^{-\tau}(2\tau)T^{\tau}(\tau) + T^{\tau}(0)T^{-\tau}(\tau)\right), \tag{8}$$

with the same eigenvalue. The eigenvectors of (8), however, give us coherent sets that are coherent on a time scale τ *both* in forward, and in backward time. The very same problem formulation (8) with three time instances has been established earlier in [12, Section 4.3], where a set was sought that is coherent in both time directions. Now, in (7) we generalize this to an aribitrary number m of time instances, such that a chain of coherent sets $M(0), M(\tau), \ldots, M(\eta)$ is sought such that each of them is coherent with both its successor and predecessor in time.

F. Meshless discretization

If the problem of time-discretization is due to the arrangement of 0-blocks in T and, as a consequence, due to disadvantageous spectral properties of T, there might be a simple solution of this problem. One can construct T in such a way that it is a dense matrix. Instead of an $(n \cdot m)$-set based discretization of space and time, one could apply a Galerkin discretization of $\mathcal{T}^\tau$ as well. In this case inner products of the form

$$T_{ij} = \langle \phi_i, (\mathcal{T}^\tau \phi_j) \rangle_\mu, \quad S_{ij} = \langle \phi_i, \phi_j \rangle_\mu, \tag{9}$$

with functions $\phi_i : \Omega \times [0, \infty) \to \mathbf{R}$ and some density measure μ of initial states have to be computed. The Schur and PCCA+ analysis has then to be based on $S^{-1}T$. If the functions ϕ_i have a global support, then these matrices are dense. The high dimensional inner products of the form (9) can be computed by Monte Carlo quadrature using trajectories with μ-distributed initial states in the space-time-domain. This kind of Galerkin discretization and Monte Carlo quadrature is widely discussed in literature. One simply has to extend the space to space-time. This approach is only applicable if trajectories of the dynamical system are available.

G. Overlapping intervals

Using the (meshless) idea of an overlapping discretization, one can also combine the pattern of (3) and (4). If the spatial discretization is based on an n-sets decomposition of Ω and the interval discretization is assumed to be overlapping, in the sense of: $[0, 2\tau], [\tau, 3\tau], [2\tau, 4\tau], \ldots$ while τ is still the discretization step, then always half of the interval "stays" and half of the interval "proceeds". For the case $m = 3$ this would turn into a transition matrix

$$T_{ol} = \frac{1}{3}\begin{pmatrix} 3T^\tau(0) & 0 & 0 \\ T^\tau(0) + T^\tau(\tau) & T^\tau(\tau) & 0 \\ 0 & T^\tau(\tau) + T^\tau(2\tau) & T^\tau(2\tau) \end{pmatrix}. \tag{10}$$

T_{ol} is a non-reversible matrix to be used for metastability analysis. The eigenvalues and eigenvectors may be complex-valued and ill-conditioned. In this case, one has to apply Schur vectors instead of eigenvectors, see Sec. II A.

H. Sparse matrices

Coherent set analysis depends on a discretization of space and time. The corresponding matrices T_p, T_{rev}, or T_{ol} can be very high-dimensional. Our meteorological data is an example for non-periodic processes. The analyzed matrices have more than 200,000 columns and rows, because the space is discretized into a grid of about 150×150 boxes. Only if the analyzed matrices are sparse and symmetric, the corresponding spectral analysis can be provided numerically. A full Schur decomposition is not feasible. Thus, for the meteorological data only approach (7) is numerically meaningful. The method how to get a sparse matrix is explained here.

The matrices $T^\tau(t)$ are dense in the described time-discretization schemes. The sparseness of the analyzed matrix can be achieved by replacing the computation of $T^\tau(t)$ with the computation of sparse matrices $Q(t)$ via the square-root approximation [24, 28]. In this approximation, the matrix element $Q_{ij}(t)$ is non-zero if and only if subset i and j

are neighbors in space. These entries are given by $Q_{ij}(t) = \sqrt{\pi(j, t+\tau)/\pi(i, t)}$, where $\pi(k, t)$ is the value of the discretized density function in set k at time t. The diagonal entries of $Q(t)$ are constructed in such a way that the row sums are zero, such a matrix is called a *generator* or *rate matrix*. The matrix $Q(t)$ is interpreted as the matrix of transition rates (not transition probabilities) between the discretization sets, and is the time-derivative of $T^\tau(t)$ with respect to τ at $\tau = 0$. In the autonomous case, generator Q and operator T^τ have the same Schur and eigenvectors. Thus, in the meterological examples, the matrices $T^\tau(t)$ in formula (7) are simply replaced by the matrices $Q(t)$ in order to yield sparse matrices. The eigenvalues with the lowest magnitude are important. In order to compute these eigenvalues and the corresponding eigenvectors, one can apply a similarity transform such that the eigenvalue problem is symmetric.

In the example of pericyclic reactions in Sec III B, which is low-dimensional, the matrices $T^\tau(t)$ are computed by the time-dependent rate matrices $Q(t)$ by the approximation $T^\tau(t) \approx I + \int_t^{t+\tau} Q(s)\, ds$. In this case, we replaced the integral by a Riemann sum of a discretization of the interval $[t, t+\tau]$ into 10 subintervals like it is suggested in [28].

III. RESULTS

A. A meteorological example analyzing a frontal structure

In the first example, the time evolution of the system is given by snapshots of density functions. We found coherent sets in precipitation data.

Hourly precipitation sums on a 2 km spaced grid stem from the novel convective scale reanalysis product COSMO-REA2 [33]. This regional realanysis has been developed in the frame of the Hans-Ertel Center for Weather Research [31]. Basis of the reanalysis product is the COSMO[26] model and a data assimilation scheme using observational nudging. As a particular novelty, REA2 assimilates rain rates derived from radar reflectivities via latent heat nudging. The horizontal spacing of 2 km permits running the model without a parametrization of deep moist convection. A corresponding product for Europe exists on a 6km grid [2].

REA2 is available for the years 2007 to 2013. Here, we analyse a moving frontal structure as a case study on Nov 11th 2007 in a time slice of 31 hours with a temporal resolution of one hour. Precipitation is considered in a rectangular box given by [8.5719, 13.0347] degrees east and [50.4271, 53.1440] degrees north, see Fig. 2.

In Fig. 2 three time slices showing the precipitation structure and the geographical distribution of the identified coherent sets are illustrated. For all three time steps three main coherent sets can be identified. In the first time step, the frontal structure lies inside a large coherent set which covers Central Europe, a second set is visualized over the northern part of the North Sea corresponding to a vortical structure behind the front. The third set is detected south of the Alps. In the second time step, the northern set moves south-eastwards with the general wind direction behind the front. The southern coherent set extends and moves in the opposite direction. In the last time step, the northern coherent set enlarges moving with the flow. In the southern coherent set, strong precipitation can be observed. On the surface pressure map in Fig. 3 provided by the German Weather Service shows the cold front passing Germany on that day. Moreover, the related surface low with closed isobars is visible which is linked to the northern coherent set. The southern coherent set is related to a high pressure system characterized by weak large scale wind velocity. To summarize, the coherent set method can identify large scale flow structures related to the meteorological concept of airmasses.

B. Analysis of a Chemical Reaction

In the following example, the mechanism of a chemical reaction is analyzed based on the time-dependence of the electron density during this reaction. We show that the choice of the time discretization scheme used for coherent set analysis can significantly influence the resulting interpretation of the dynamics. The final interpretation of the process depends critically on the choice of the discretization and without further information, it is not clear which discretization scheme leads to coherent sets that correctly represent the considered process.

Our example is the determination of the mechanism of a chemical reaction. Fig. 4 shows the reaction of interest, double-proton transfer in the formic acid dimer, in terms of Lewis structures of reactants R and products P. Letters denote the respective nuclei, while connections denote chemical bonds, i.e. electrons "shared" between the nuclei. Knowledge of the reaction mechanism means knowledge of the motion of the electrons during rearrangement of the molecular structure. The reaction is an example of a pericyclic reaction, i.e. a reaction happening in one step and in a circular way. There are many possible ways of how this reaction may occur, depending on the specific environment. We restrict ourselves to the case of coherent tunneling where it is assumed that the system can be described as

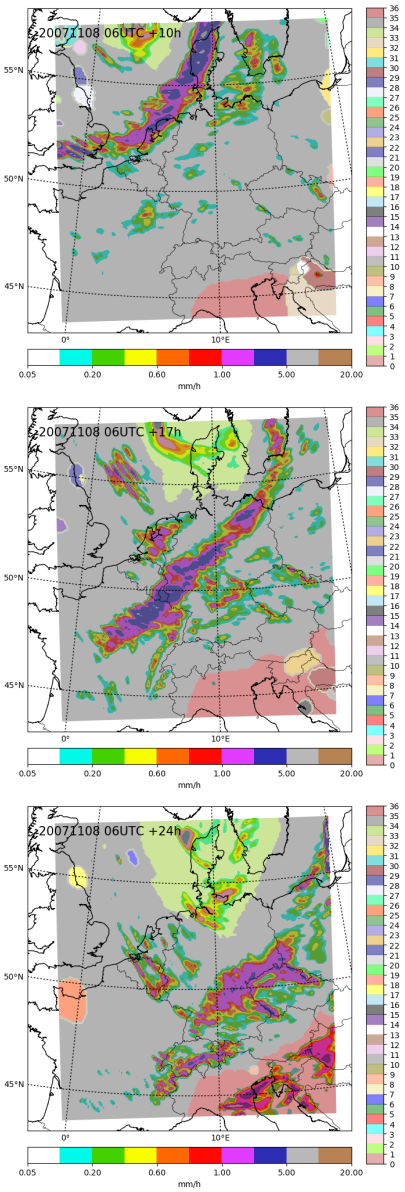

FIG. 2. Precipitation in mm/h from REA2 and identified coherent sets for November 8th 2007, 16 UTC (top) November 8th 2007, 23 UTC (middle) and November 9th 2007, 06 UTC (bottom)

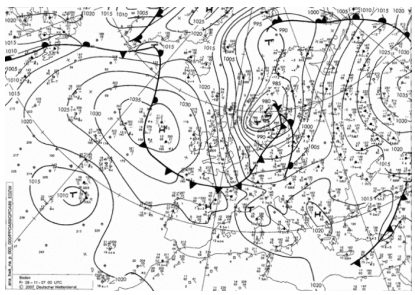

FIG. 3. Surface pressure map of Nov 9th 2007 00 UTC provided by the German Weather Service

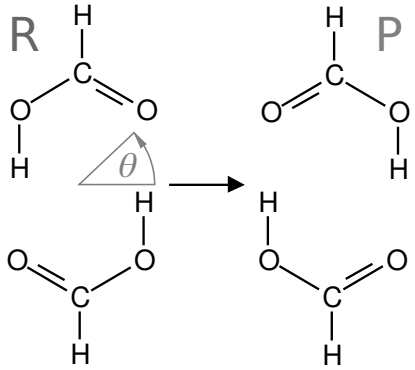

FIG. 4. Schematic drawing of double proton tunneling in the formic acid dimer. During the reaction from reactants R on the left to products P on the right, the H nuclei attached to an O nuclei of one formic acid molecule move to the O nuclei of the other one. During that process the electron density also changes accordingly. The angle θ along which the radial electron density is measured is also shown.

a superposition of the lowest two (almost degenerate) states of the respective molecular Hamilton operator in the non-relativistic approximation.

Typically, for small molecules like the formic acid dimer, it is possible to obtain the time-dependence of the electron density (the probability density of finding an electron at a certain location in space) for the reaction to a good approximation. However, to find the reaction mechanism, it is necessary to know the electronic flux density or current density, a vector field that describes how the electrons move from one instant of time to the next. In contrast to the electron density, the flux density is much harder to compute [1]. Hence, we investigate if an analysis of the time-dependent electron density alone with PCCA+ can be used to obtain information about the reaction mechanism, without explicit knowledge of the flux density.

For this purpose, we describe the tunneling process with a quantum mechanical two-state model similar to that described in [15]. The electronic structure of R is determined from a Hartree-Fock calculation with a cc-pVTZ basis set [20] using the program package Molpro,[36] and the program Orbkit[16] was used to calculate the electron density of R. Although more advances methods for calculating the electronic structure of this molecule are available, the Hartree-Fock method suffices for the present purpose. The structure and electron density of P is given by the requirement of conservation of angular momentum during the change from R to P. The time-dependence of the electron density is given analytically in the 2-state model. As the reaction is a cyclic rearrangement, we use cylindrical coordinates and consider only the angular density, i.e. we integrate the electron density along all but the angular coordinate given in Fig. 4. Then, the hope is that information about the reaction mechanism can be obtained from analyzing the dynamics of this angular density alone. For further details, see [28].

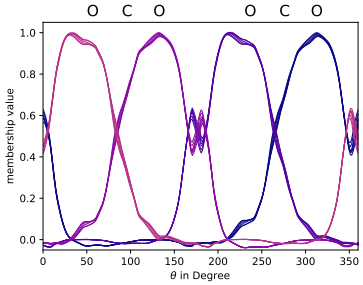

FIG. 5. Time-dependent membership functions for the angular electron density with reversible discretization (7). At each of the six time steps there are four such functions. Note that the membership functions at different times vary little and their difference is barely visible in the figure. Above the figure, the approximate angular location of the C and O nuclei is indicated.

The time-dependence of the radial electron density $\pi(t)$ is represented by a time-dependent transfer operator $\mathcal{P}^\tau(t)$ in the sense of an ensemble-based approach and analogously to the square-root-approximation used for the precipitation data. For the time-discretization, we apply the scheme of equation (7). Starting from the initial electron density, we aim at determining coherent sets that reveals boundaries in $\Omega \times [0, \theta]$ which are rarely crossed by "trajectories", i.e. where there is little electron flux. From those, information about the reaction mechanism can be extracted. Fig. 5

shows the membership functions for this case together with the approximate angular position of the C and O nuclei. Two of the boundaries between membership functions correspond to angles where the C nuclei are located ($\theta = 90°$ and $\theta = 270°$), while the other two boundaries correspond to the center of the path connecting the initial and final position of the H nuclei ($\theta = 0°$ and $\theta = 180°$). Consequently, from this analysis we would conclude that there is little electronic motion through the surfaces corresponding to these angles, implying a motion of the electrons such that they do not cross these surfaces.

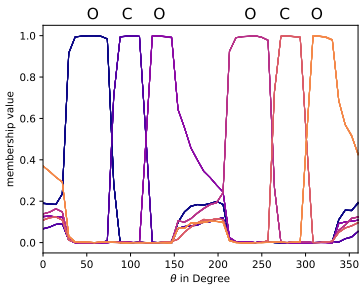

FIG. 6. Time-dependent membership functions for the angular electron density with non-reversible discretization (10). At each of the ten time steps there are six such functions. Note that the membership functions at different times vary little and their difference is not visible in the figure. Above the figure, the approximate angular location of the C and O nuclei is indicated.

Although the molecular structure in Fig. 4 only has cyclic symmetry, the resulting membership functions in Fig. 5 have cyclic symmetry *and* an additional mirror axis at 180°. This additional symmetry is due to making the matrix reversible. If the discretization scheme T_{ol} of (10) is applied, the membership vectors resulting from PCCA+ and Schur decomposition are very different, see Fig. 6. There is a cyclic symmetry but no mirror symmetry, and instead of four membership functions there are now six, one at the location of each of the heavy atoms C and O. Hence, in contrast to the previous analysis where little fluxed at the location of the C nuclei were expected, now there is an angular area corresponding to the region of the C nuclei where the membership function is close to 1, i.e. where a lot of electron flux is expected. However, we also note that coherent tunneling is an oscillatory process, i.e. after changing from structure R to structure P, the system would change back to structure R. Consequently, we would expect a stronger time-dependence of the membership functions, because we expect a continuous transition from the forward to the backward reaction, where the latter is given by the mirror image of Fig. 5 with mirror axis $\theta = 180°$.

IV. CONCLUSION

The concept of metastability can directly be transferred to a mathematical framework for coherent sets. This generalized concept uses transfer operators on extended state space, pioneered in [9], that can be approximated from trajectories as well as analyzing the time-evolution of density functions (as focused on in this paper). Whereas metastable sets are constant in time, coherent sets move in time. These two types of sets can be identified in terms of membership functions from a PCCA+ analysis of the corresponding transfer operators. The main remaining question is, how to discretize the space-time-domain. Space and time usually have different physical meanings, hence hybrid discretization schemes seem fitting [9, Section 7.4]. Sometimes there are algorithmic issues, which determine the choice of the approach used. Discretizations which artificially produce reversible Markov chains for better spectral properties, however, might introduce symmetries into the system which are not physically justified. The application of spectral approaches (like PCCA+ with Schur vectors) combined with the square-root-approximation for analyzing coherent sets of time evolving density functions is a novel method suggested in this article. It has a broad range of applicability which has been shown by two very different examples.

V. ACKNOWLEDGEMENT

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