Directed graphs of structurally stable potential energy surfaces representing *a-priori* reaction pathways

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An intrinsic property of potential energy surfaces (PES) that holds within the adiabatic approximation is established: its structural stability.

We derive the condition that ensures this property: There cannot be any integral curve of the gradient field of the PES that connects two classical transition state configurations without passing through another critical configuration in between.

Under this situation, we can establish a one-to-one correspondence: a whole class of adiabatic PES defining one reaction mechanism is associated to a directed graph. Thus, the problem of finding *a-priori* pathways involving a given number m of chemical species narrows down to a classifying certain directed graphs with m sinks. The combinatorial method is derived in this paper.

Detailed examples on *a-priori* pathways for degenerate thermal rearrangements and on 1–2 hydrocarbon shifts are worked out and found in agreement with experimental evidence.

Key words: Intrinsic reaction coordinate—transversality condition on the separatrices—graph representation of a planar dynamical system

1. Introductory remarks and definitions

We shall be concerned with adiabatic potential energy surfaces (APES) $U = U(x)$, x belongs to the Nuclear Configuration Space, where $U(x)$ is the standard adiabatic potential under the Born–Oppenheimer approximation ([1]).

Although the nuclear configuration space is infinite, it is clear that at the free atom dissociation limit: $x \dashrightarrow \infty$, the potential U increases monotonically tending asymptotically to the zero limit.

Therefore it is always possible to consider a disc $x \leq R$ for sufficiently large R, so that at the boundary of the disc the gradient force field $y = -\mathrm{grad}_x U$ points inwards.

Henceforth $y(x)$ will be named the standard adiabatic vector field and abbreviated SAVF.

The SAVF preserves the disc. That is, if we follow the integral curves of $y(x)$ tangent at every point x to the vector $y(x)$, we find that we never leave the disc if we start in any point belonging to it.

Within the adiabatic approximation, the SAVF y should remain "qualitatively the same" under C^1 (first differentiable)-perturbations.

By "qualitatively the same "we mean that by calling q the perturbed vector field, there exists a homeomorphism (bijective and bicontinuous map) $T: \mathcal{D} \dashrightarrow \mathcal{D}$ ($\mathcal{D}$ is a compact region preserved under y) mapping the trajectories of y onto those of q.

In other words: A SAVF y is structurally stable in the sense of Adronov and Pontriagin ([2], for applications of this result in chemical dynamics the reader is referred to our paper [3]).

Therefore, it becomes natural to find and classify the APES up to the homeomorphisms T's.

For arbitrary y and q so that T exists, we shall write $y \sim q$.

As we shall demonstrate in Sect. 3, finding the classes modulo $\sim$ for a given number of minima in the APES is exactly equivalent to finding the *a-priori* mechanisms in processes involving chemical species in correspondence with these minima.

Thus, the classification of potential energy surfaces and their gradient vector fields up to T's vis-à-vis the critical points as done in the present paper, provides an alternative and more detailed approach to the purely combinatoric or graph theoretic classification and enumeration of all possible mechanisms of given overall reaction.

This was done previously by one of us (O. Sinanoglu [4], [5], [6].)

Some definitions are required to show that the classes modulo $\sim$ are in one-to-one correspondence with the *a-priori* mechanisms.

A *saddle point σ of index n* of the SAVF y is a critical configuration (*a* zero of y) such that the dimension of the manifold of outgoing trajectories is n. This manifold is tangent at σ to the plane of unstable vibrational modes of that nuclear arrangement. The classical transition states are saddles of index 1.

Further research is being done by these authors to elucidate the nature of elementary reactions involving a transition species with more than one promoting mode.

The integral curves joining saddles with sinks of y are the *intrinsic reaction coordinate curves* (IRC) (the concept was developed by Fukui [7] and Fukui and Tachibana; see for example [8], [9]).

The integral curves joining sources to saddles are the *separatrices* (see [10] for terminology).

The *basin of attraction* (or simply *basin*) of any critical configuration is the manifold of trajectories tangent to the stable vibrational modes of that species at that configuration. (The whole manifold is defined by a local property).

The IRC's and separatrices are tangent to the unstable and stable planes of vibrational modes of the transition state config. respectively.

Now we can state that the one-to-one correspondence exists since the only two features of an APES required to determine its class modulo $\sim$ are: (c.f. Sect. 3)
a) The set of IRC's.
b) The set of separatrices. This set determines the boundaries of all the basins of the chemical species (the sinks of y). In Sect. 3 we shall prove that two SAVF's y and q are equivalent if and only if they present:
a') The same set of IRC's up to homeomorphisms T's. That is, the set of IRC's of y can be continuously deformed onto that of q.
b') The same pattern of separatrices up to homeomorphisms T's.

Once we know the topology of these two sets, we can build a directed graph which will be called the IRC's-and-separatrices (IRCS) graph:

Each vertex of the graph corresponds to a critical configuration and each edge corresponds to an IRC or a separatrix.

$\partial \mathscr{D}$ is regarded as a source of the SAVF and shows up as a vertex in the graph.

The IRCS graph plays a central role in classifying the *a-priori* SAVF classes within a given number of chemical species. A necessary condition for two SAVF to belong to the same class is that they present the same IRCS graph.

In Sect. 3 we shall prove that the problem of finding the classes modulo $\sim$ is equivalent to the combinatorial problem of finding the isomorphism classes of IRCS graphs so that these isomorphisms preserve certain distinguished subgraphs.

As an introductory illustration consider an isomerization $ABC \rightleftharpoons BCA$ with a single transition state (an example of this process is the H 1–2 shift in the species $[CH_2CH_3]^+$) ([11]).

Since there is no stable intermediate in between the two basins of the two tautomeric forms, the SAVF up to homeomorphisms T's is displayed in Fig. 1 as well as the associated IRCS graph.
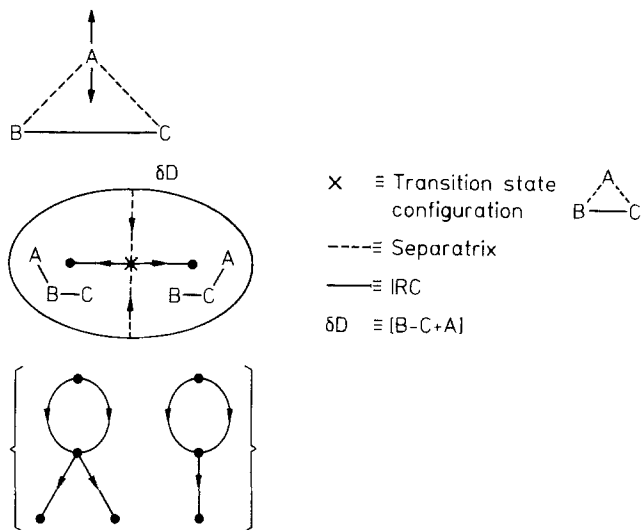
Fig. 1

The two regions of $\mathcal{D}$ limited by the separatrix are the basins of the tautomers ABC and BCA. Let us consider the IRCS graph:

The upper edges correspond to the separatrices, that is, the integral curves tangent to the direction of the stable vibrational mode of the transition state at this precise nuclear configuration:

The lower edges correspond to the IRC-curves tangent at the transition state to the promoting vibrational mode.

Any 1–2 shift via a single transition state lies in the same class modulo $\sim$.

In the rest of the paper we shall find the necessary and sufficient conditions that ensure the structural stability of an APES (Sect. 2), solve the classification problem (Sect. 3) and provide further and detailed chemical examples (Sect. 4).

2. Structural stability of adiabatic potential energy surfaces

The conditions that ensure the structural stability (as defined in Sect. 1) of an adiabatic PES require a previous description of the stable and unstable manifolds of trajectories passing through a transition state configuration σ.

The stable manifold of σ is, roughly speaking, the manifold of trajectories having σ as a sink.

It is rigorously defined as the set of points p's in $\mathcal{D}$ for which the integral curve through p which solves the system of differential equations:

$$\frac{dx_i}{\dfrac{\partial U}{\partial x_i}} = \frac{dx_j}{\dfrac{\partial U}{\partial x_j}} \qquad i > j \tag{1}$$

tends to σ as we follow the field of directions $y(x)$ (which associates a direction given by $y(x)$ to each point x in $\mathscr{D}$).

This stable manifold is denoted $M^s(\sigma)$. This is the manifold of integral curves tangent at σ to the plane of stable vibrational modes of σ. In the case of the example depicted in Fig. 1, $M^s(\sigma)$ consists of the separatrix joining the source $BC + A = \partial\mathscr{D}$ to the triangular configuration σ.

$M^u(\sigma)$ denotes the unstable manifold which is the collection of trajectories that have σ as a source (they tend to σ as we follow the field of directions $-y(x)$). $M^u(\sigma)$ is tangent at σ to the plane of unstable vibrational modes of σ.

In the case of the 1–2 shift described in Fig. 1, $M^u(\sigma)$ is the IRC curve joining the two minima (sinks of $y(x)$).

If, as in Mezey's catchment regions (see for example [12]), a chemical species is defined as the minimum jointly with its associated basin, the definition of transition state should be also extended: the *generalized transition state* is defined as σ jointly with $M^s(\sigma)$ (its "basin"). This region defines the boundaries of the basins of two minima.

These two definitions can be contrasted with the older notion of "significant structures ([13]) which corresponds to a piece of the stable manifold: the bottom of the basin. This is not a mathematically well defined notion.

In general, for a configuration space of dimension higher than 2, there could exist nonclassical transition states such that dimen $\cdot M^u(\sigma) > 1$. Again the generalized transition state is defined $M^s(\sigma)$. Further problems arising when treating nonclassical transition states will be studied in a separate paper.

The set of separatrices determining the distribution of the different species is now defined as $\bigcup_\sigma M^s(\sigma)$ where the union extends through *all* the transition states σ. This set is then the union of all the generalized transition states.

The pattern of IRC's defining the coupling of pathways for all the elementary steps is rigorously defined as $\bigcup_\sigma M^u(\sigma)$.

Now we can state those conditions that a SAVF should obey to ensure its structural stability.

Since the SAVF are gradient fields, no integral curve is a closed orbit, therefore the conditions are:
1) The Hessian matrix $(\partial^2 U/\partial x_i\,\partial x_j)$ has no eigenvalue with zero real part at any critical configuration in $\mathscr{D}$.
2) Consider any two transition states σ_1, σ_2. Then the manifolds $M^s(\sigma_1)$ and $M^u(\sigma_2)$ are *transversal* ([10], [14]) and so are $M^u(\sigma_1)$ and $M^s(\sigma_2)$. This condition means that either they are disjoint or for every p belonging to $M^s(\sigma_1) \cap M^u(\sigma_2)$ the tangent spaces of $M^s(\sigma_1)$ and $M^u(\sigma_2)$ at p span the whole R^n ($n =$ dimension of the nuclear configuration space):

$$t_p M^s(\sigma_1) + t_p M^u(\sigma_2) = R^n \tag{2}$$

an analogous statement is valid for $M^u(\sigma_1)$ and $M^s(\sigma_2)$. For all p in $M^u(\sigma_1)$ and in $M^s(\sigma_2)$,

$$t_p M^u(\sigma_1) + t_p M^s(\sigma_2) = R^n. \tag{3}$$

For a chemical interpretation of these results let us consider a 2-dimensional cross-section of the APES involving the directions of the promoting (unstable) mode at σ_1 and a stable normal mode of σ_1. Then our transversality condition can be stated in the following

Theorem I: Consider a two dimensional cross section of the APES: $U = U(x_1, x_2)$. Let σ_1 and σ_2 be two transition state configurations, then there is no separatrix joining σ_1 and σ_2 without passing through a source. This result can also be stated as follows:

The promoting mode at one transition state cannot be deformed along the meta IRC tangent to it to become the stable mode of another transition state.

Proof: If such a connection exists, then, for any p in the separatrix, we get one of the following relations:
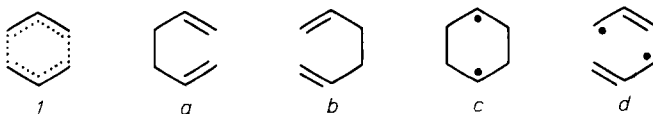
$$t_p M^s(\sigma_1) + t_p M^u(\sigma_2) = R \tag{4}$$

$$t_p M^u(\sigma_1) + t_p M^s(\sigma_2) = R. \tag{5}$$

(Since this meta-IRC belongs simultaneously to $M^s(\sigma_1)$ and $M^u(\sigma_2)$.)

Therefore the tangent vectors at p coincide and the transversality condition does not hold.   Q.E.D.

As an example to exhibit the restrictions imposed on an APES by the structural stability condition consider the APES for the degenerate Cope rearrangement ([15], [16]).

The basic problem consists in deriving the topology of the boundaries of the two minima in the APES (the two sinks of the SAVF) a and b. That is describing $\bigcup_\sigma M^s(\sigma)$.

The structural stability restriction on APES *implies that the biradicals c and d which are directly connected to the concerted transition state 1 (see* [15]*) cannot be also transition states (otherwise we would have a saddle–saddle connection of the* SAVF*) but they should be maxima in this cross section.*

Moving along the separatrix, starting from the saddle *1* towards the dissociated atoms limit, the biradical configurations cannot be the last critical structures to be found since the SAVF points inwards as we move towards the limit $x \rightarrow \infty$. Therefore, there exists at least one saddle point after each biradical configuration.

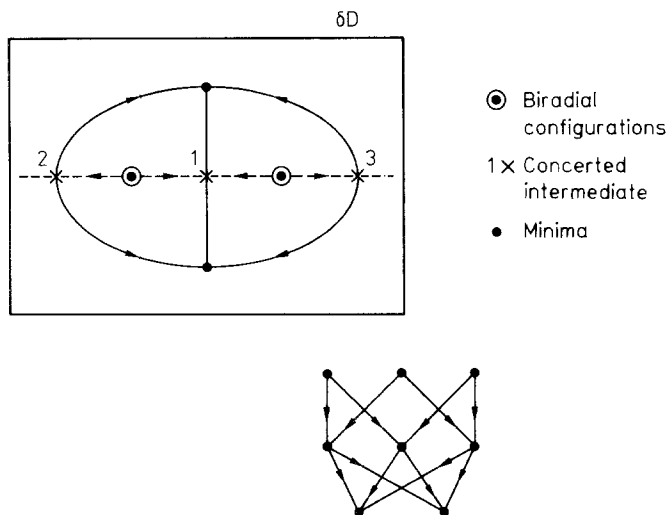Up to homeomorphisms T's, the SAVF is displayed in Fig. 2.

6D

⊙ Biradial
   configurations

1× Concerted
   intermediate

● Minima

Fig. 2

3. The topological classification of adiabatic potential energy surfaces using directed graphs

As previously shown, the IRCS graph is built for two dimensional cross sections of the APES. It contains all the topological information on the set of IRC's: $\bigcup_\sigma M^u(\sigma)$ and on the set of separatrices (or the union of generalized transition states) $\bigcup_\sigma M^s(\sigma)$.

Certain subgraphs of the IRCS graph need to be considered.

These are obtained by simultaneously removing a pair of vertices in the IRCS graph; one corresponding to a chemical species (a sink) and the other to a source and removing also all the pathways joining these two vertices.

These subgraphs are displayed in Fig. 3.

The distinguished subgraph of the IRCS graph considered in the Sect. 1 is of the type II.

The existence of a distinguished subgraph of the type I implies that at least two elementary steps are coupled since the sink representing the chemical species presents two incoming edges corresponding to two different transition states.
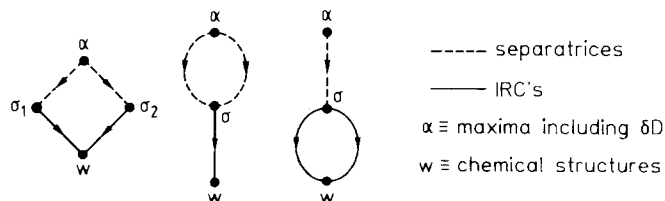

----- separatrices

——— IRC's

$\alpha \equiv$ maxima including δD

$w \equiv$ chemical structures

Fig. 3

The generalized transition state in subgraph II (that is, the two separatrices-edges joining the source to the saddle) determines two regions in $\mathscr{D}$, one contains the source with associated vertex in the subgraph II.

In a subgraph of the type III we have two IRC-edges joining a saddle to a sink; this indicates that there exist two loci for the same reaction.

The collection of the IRCS graph of a SAVF $y(x)$ denoted $G(y)$ and its distinguished subgraphs is called the IRCS* graph and it is denoted $G^*(y)$. If there exists an isomorphism $G(y_1) \sim G(y_2)$ preserving distinguished subgraphs, we will write $G^*(y_1) \sim G^*(y_2)$.

The following theorem shows that the problem of finding the *a-priori* mechanisms for a given number of chemical species is reduced to the combinatorial problem of finding the IRCS* graphs with that given number of sinks and saddles.

Theorem II: If two standard adiabatic vector fields $y_1(x)$, $y_2(x)$ have isomorphic IRCS* graphs: $G^*(y_1) \sim G^*(y_2)$, then these vector fields are equivalent modulo $\sim$, therefore they determine the same mechanism.

Proof: Peixoto ([17]) has considered the following graph together with the distinguished subgraphs associated with any structurally stable vector field $y(x)$: At each saddle vertex we draw two incoming edges to σ from vertices α for which there exists a trajectory of $y(x)$ leaving α and entering σ and we draw two outgoing edges from σ to vertices ω for which there is a trajectory leaving σ and entering ω. These graphs have the property that if two such graphs are isomorphic and the isomorphism preserves all the distinguished subgraphs, then the respective vector fields are equivalent modulo $\sim$. If $y(x)$ is the SAVF of an APES, the trajectories determining the edges in the Peixoto's graphs have an extreme chemical significance since they are respectively the separatrices of the basins of attraction of the chemical structures and the IRC curves. Therefore we get the following implication:

$$G^*(y_1) \sim G^*(y_2) \Rightarrow y_1 \sim y_2.$$

Now we can develop the combinatorial method for determining the IRCS* graphs with given overall reaction and given number of sinks.

The restrictions that a directed graph with m sinks should fulfill to be an IRCS graph representing a mechanism with m (stable) chemical species are the following:

I') The vertices in the graph corresponding to transition state configurations have exactly two incoming and two outgoing edges.

II') No edges occur between sinks and sources except if there is only one sink, only one source and no saddles.

III') The numbers of the different kinds of vertices are subject to the following Morse relation ([17], [18]):

$$m - s + M = 2 \tag{6}$$

s = number of saddle critical points of the SAVF $y(x)$. M = number of sources, including $\partial\mathcal{D}$.

To prove the formula (6) for IRCS graphs consider the vector field $y(x)$ restricted to the region $\mathcal{D}$.

Since $y(x)$ points inwards along the boundary $\partial\mathcal{D}$, we can regard $y(x)$ as a vector field defined on the n-sphere (we recall the reader that n is the dimension of the nuclear config. space).

The boundary $\partial\mathcal{D}$ becomes a source in the n-sphere ([17], [18]).

The Poincare–Hopf formula for vector fields defined on a smooth compact manifold relates the alternative sum of the different numbers of critical points to the Euler characteristic X of the manifold.

The critical points of $y(x)$ are, as we have seen in one-to-one correspondence with the vertices of the IRCS graph, therefore

$$m - s = M = X = 2 - 2g. \tag{7}$$

Relation (7) is only valid for orientable manifolds with genus g ([17], [18]).

For the n-sphere we have $g = 0$, therefore the relation (6) is proven.

These graphs could also be treated as "networks" of two kinds of undirected lines and three kinds of vertices by the methods of Sinanoglu ([6]) who developed the 1- and 2-topology of networks of two kinds of lines and three kinds of vertices.

4. Example
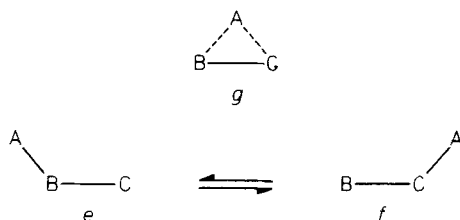
The 1–2 shifts in carbonium ions for which a general scheme is provided above, follow two general pathways
a) The triangular intermediate g is a transition state of index one (that is a classical transition state) and the $M^s(g)$ is the separatrix of the basins of the two sinks e and f.

This case is illustrated in the H shift of the species $CH_3CH_2^+$ and it was briefly discussed in Sect. 1 (see [11]).
b) The triangular intermediate is a minimum of the APES. This case can be illustrated in the CH_3 shift in the species $CH_3CH_2CH_2^+$ ([19]).

We shall calculate the *a-priori* mechanisms in this situation restricting ourselves to two and three classical transition states (c.f. [19]), that is, $s = 2$ or 3.
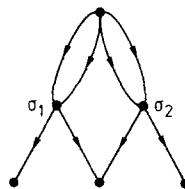
Fig. 4

If $s = 2$, then $M = 1$ from the index formulas (6) and (7).

There is only one possible IRCS graph which is displayed in Fig. 4. It is the only directed graph fulfilling I'), II') and III') with three sinks and two saddles.

The two generalized transition states $M^s(\sigma_1)$ and $M^s(\sigma_2)$ separate the basins of e from that of g and that of g from that of f respectively. They are represented by the upper four edges in the graph. The only maximum is $\partial \mathscr{D} = BC + A$.

In the case of three transition states, from the index formulae (6) and (7) we have two maxima.

The *a-priori* mechanisms are again represented by the IRCS graphs with three sinks and three saddles. The four of them are displayed in Fig. 5.

The topology of the APES where both reaction pathways a) and b) are present for the reaction is given by the only IRCS graph with three sinks and three saddles but with overall reaction
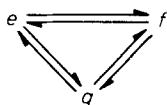
This IRCS graph is displayed in Fig. 6. It cannot present distinguished subgraphs of the type II' since each sink should be connected to two different saddles.
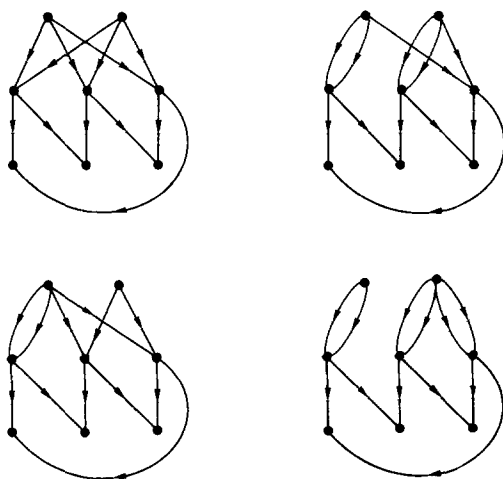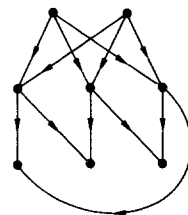

Fig. 5

Fig. 6

The pattern of the separatrices is therefore the same as in the IRCS graph in Fig. 5 number 1.

This graph corresponds mechanistically to the overlap of two pathways with corresponding IRCS graphs given in Figs. 1 and 4.

Within the STO-3G level of approximation, there is only one saddle point detected in the CH_3 migration in the species $C_3H_7^+$ ([19]). The single saddle actually resolves in a set of two saddles and one sink in between. These three critical configurations being very close to each other. The triangular intermediate forms an "Eyring lake" shallow minima in the APES. The virtual process of resolution of the saddle is reflected in the change in the associated IRCS graphs as displayed in Fig. 7.
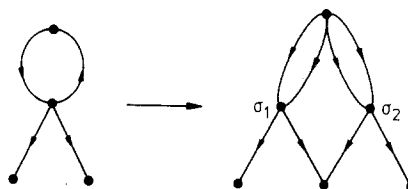

Fig. 7

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