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Saddle points of index 2 on potential energy surfaces and their role in theoretical reactivity investigations

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After a general characterization of "second order" saddle points two boundary cases are derived and illustrated by examples. The utilization of the classification is pointed out. One type, the virtual saddle point of index 2 (V-SP 2), may be understood as "geometrical" superposition of two saddles of index 1 (transition structures) which belong to relatively independent processes within the chemical system.

Key words: Potential energy surface—Theory of chemical reactivity—Saddle points of index 2—Descent and decomposition vectors

1. Introduction

The essential point in transition state theory (TST [1] is the formulation of the transition state. Taking the concept of potential energy surfaces as the basis of that theory transition states correspond to saddle points of index 1 (SP 1, the expression "first order saddle point" is also used in the literature) on the surface $E = f(x)$ of the chemically reacting system. (It is well known that this function in general is not given analytically, but has to be calculated point by point through iterative solution of matrix eigenvalue problems arising from the application of LCAO MO SCF methods). Saddle points belong to the so-called stationary points (with the coordinate vector x^{st}) on the potential energy surface (PES). In these points the gradient of the potential energy $g = \nabla E$, vanishes

$$\boldsymbol{g}(\boldsymbol{x})\Big|_{\boldsymbol{x}=\boldsymbol{x}^{st}} = 0 \qquad \text{with} \qquad g_r = \frac{\partial E}{\partial x_r}. \tag{1}$$

The stationary points are now characterized by the Cartesian force constant matrix $\boldsymbol{F}$

$$F_{rs} = \frac{\partial^2 E}{\partial x_r \partial x_s}\Big|_{\boldsymbol{x}=\boldsymbol{x}^{st}} = \frac{\partial g_r}{\partial x_s}\Big|_{\boldsymbol{x}=\boldsymbol{x}^{st}} \tag{2}$$

which has one and only one negative eigenvalue in the case of a saddle point of index 1 (transition structure). The observation of two negative eigenvalues of the force constant matrix in a stationary point on the surface indicates the existence of a saddle point of index 2 ("second order saddle point"). Stationary points with zero eigenvalues, occuring in addition to the 6(5) due to translation and rotation, should not be confused with saddles of a higher index and are not included in our discussion (cf. "monkey saddles" [2]).

Negative eigenvalues measure the negative curvature along the principal axes on the PES in a stationary point. Their eigenvectors indicate the corresponding atomic shifts for leaving the saddle. A vibrational analysis according to Wilson [3] requires mass weighting of the Cartesian force constant matrix. Within the scope of that theory the negative eigenvalue $-\lambda_j$ of this matrix represents an imaginary vibration ν_j^i (decomposition mode [2]) in a generalized harmonic vibrational problem. With $-\lambda_j = (2\pi c\nu_j)^2$ we have

$$\nu_j^i = \frac{1}{(2\pi c)} i\sqrt{\lambda_j} \qquad \text{where } i = \sqrt{-1}. \tag{3}$$

Each decomposition mode (d-mode) is as any other normal mode characterized by an eigenvector (d-mode vector) assigning the displacement coordinates along the imaginary vibration. It should be stressed that the d-mode vector does not describe atomic shifts due to the properties of the PES alone, but is modified including the masses in the kinetic energy terms (cf. also [4]). So, in walking on PES we should consider the eigenvalues and corresponding eigenvectors. We denote the negative eigenvalues of the Hessian matrix as dc(descent)-characteristic and their eigenvectors as dc-vectors in distinction to the notation given above for imaginary vibrations. In the literature [5] the term "transition vector" is also used for the dc-vector of a saddle point of index 1.

Large imaginary frequencies refer in general to high lying saddle points. But in the reversed situation small amounts of imaginary frequencies cannot necessarily be interpreted as belonging to low lying saddle points. Here the saddle may be broad (cf. also [6]).

A saddle point of index 1 is a lowest path maximum in a valley which is defined at least in the neighbourhood of the saddle point. Saddle points of second or higher order may be illustrated as maxima (hilltops) in the subspace of the eigenvectors (coordinates) connected with the negative eigenvalues. They do not appear as entities in theories of chemical reactivity, that is, they are not located on minimum energy paths (MEP) of PES. There are always pathways of lower energy leading "around" saddles of a higher index [7]. These are the reasons for saddle points of index 2 and higher indices being mainly mentioned for completeness in PES investigations (see for instance [8a]). It should be noted that they were also used in a general critical point analysis of multidimensional PES (cf. [8b]).

In the following we derive two types of saddle points of index 2 as boundary cases and discuss their meaning in theoretical reactivity investigation. For a better understanding of the consequences for the computational practice we shortly review some methods for the localization of stationary points on PES.

2. The localization of saddle points

We classify the common methods as follows:

A) Descent methods on the PES (variable metric minimization methods) [9, 10];
B) nonspecific methods which calculate all types of stationary points (e.g. descent methods on a σ-surface defined by the gradient norm [5]);
C) ascent methods of different kind [11, 12], for a review see for example [13].

To A): These methods localize saddle points only by using their properties of symmetry conservation [9]. Hence, if the symmetry is decreased along the d-mode(s) of the saddle point structure, the point group is suitable for localizing the saddle by descent on the PES. The basic type of these methods is given by

$$\boldsymbol{q}^{n+1} = \boldsymbol{q}^{n} - \alpha_n \boldsymbol{A}^n \boldsymbol{g}^n_{\mathrm{PES}}, \qquad \boldsymbol{g}_{\mathrm{PES}} = \boldsymbol{\nabla} E \tag{4}$$

$\boldsymbol{q}^n$ is the vector of coordinates in the nth iteration. $\boldsymbol{A}$ represents an approximation to the inverse Hessian matrix $\boldsymbol{H}^{-1}$ of the PES (which is positive definite) starting usually with the unity matrix (steepest descent) followed by calculations using simple update schemes. α is a step length parameter. Symmetry conservation additionally ensures a high degree of accuracy for geometry and energy data.
To B): The calculation of saddle points as well as any other stationary point on the PES may be realized on the σ-surface [5]

$$\sigma(\boldsymbol{q}) = 1/2\boldsymbol{g}^T_{\mathrm{PES}}\boldsymbol{g}_{\mathrm{PES}} = 1/2\sum_r g_r^2(\boldsymbol{q}) \tag{5}$$

which is defined by the Euclidian norm of the gradient. Using all experience of descent and least square methods, this procedure becomes very effective. Symmetry conservation is only possible by special symmetry constraints in the atomic coordinates.

To C): This type of method was developed for a direct calculation of saddle points of index 1. The method works if one can ensure that the minimum energy path is at least qualitatively of the so-called "valley path type" [14].

3. The "Proper Saddle Point of Index 2" (P-SP 2)

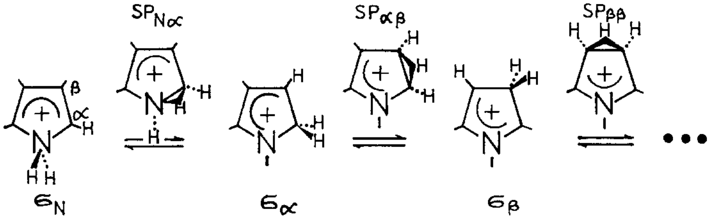
In this case we find two directions of negative curvature with eigenvectors which concern the same atom (or the same group of atoms) of the system if we look for the important components of the vector. The saddle point structure may be abandoned by moving the atom (or the atoms) along one of the two directions of negative curvature or in any other direction between them. In this way we reach the other neighbouring stationary points: minima or SP 1(SP 2). A d-mode of such a further saddle point (as next neighbouring stationary point to the given P-SP 2) has nothing to do with the d-modes at the given original P-SP 2.

In the following we discuss examples for P-SP 2 exhibiting relatively high energy differences to other stationary points in their neighbourhood. Such types of P-SP 2 are very illustrative and of indirect importance for the prediction of chemical reaction pathways. All calculations were carried out with the well-known MINDO/3 method [15]. It should be stressed that the conclusions in our paper do not depend on the type of quantum chemical method. Furthermore, the selected examples represent qualitatively correct theoretical gas phase results.

First example: *face protonated pyrrole-*H^+

In the electrophilic attack on aromatic compounds face cationization plays an important role in the discussion of possible reaction paths. Li^+, Na^+ etc. form minima on the PES in the face arrangement (centrosymmetrical association) [16, 17], but cations like H^+, CH_3^+, F^+ etc. form unfavourable structures which represent typical P-SP 2 [16, 18-20].

Face protonated pyrrole, which cannot be localized by modifications of method A but by methods B and C, shows two strong d-modes $\nu_1^i = 2700i\ \mathrm{cm}^{-1}$, and $\nu_2^i = 2834i\ \mathrm{cm}^{-1}$ both indicating a shift of the central proton to the periphery of the ring system (Fig. 1, Table 1). We reach the σ-complex minima going downhill on the PES from the face protonated structure. The σ_α-complex is here more stable by $\Delta E_{\mathrm{pot}} \approx 405$ kJ/mol. Using symmetry conservation (method A) we can move the proton in the symmetry plane bisecting the ring towards a SP 1 of structure $SP_{\beta\beta}$. The other transition structures of the proton shifts ($SP_{\alpha,\beta}$ and $SP_{N,\alpha}$) have no suitable symmetry elements to use symmetry conservation. The calculation of these SP requires a searching by methods of the B and C type.



Details of the interesting proton shifts on pyrrole were published recently [20]. A qualitative illustration of the energy maximum arising from proton migration over the pyrrole ring can be found in an earlier paper [21].

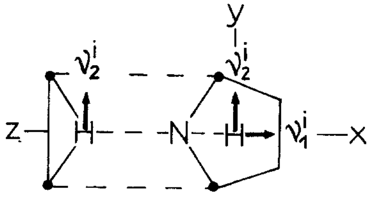


Fig. 1 Illustration of the descent and d-mode vectors, respectively, of face protonated pyrrole (NC_4H_5)

Table 1. Imaginary frequencies and displacement vectors[a] of face protonated pyrrole as a proper second order saddle (P-SP 2) on the PES

Atoms/ coordinates[b]		$-\lambda_1$ dc-vector	$\nu_1^i(2834i\ \mathrm{cm}^{-1})$ d-mode-vector	$-\lambda_2$ dc-vector	$\nu_2^i(2700i\ \mathrm{cm}^{-1})$ d-mode-vector
N	y	—	—	−0.24	—
	z	−0.30	—	—	—
C_α	x	−0.20	—	—	—
$H^\oplus$	x	0·85	0.97	—	—
	y	—	—	0.88	0.98

[a] Descent and d-mode vectors; only components $\geqslant 0.2$ are listed. The sign of the components may be changed: such a "phase change" represents the alternative direction of descent

[b] cf. Fig. 1

Second example: *face protonated benzene*

This P-SP 2 is best calculated by symmetry conservation (method A). The structure exhibits two *degenerated* decomposition modes:

$$\nu_1^i = \nu_2^i = 2542{,}5i\ \mathrm{cm}^{-1}.$$

It is well-known that in the case of degenerated eigenvalues $\lambda_1 = \lambda_2$ the eigenvectors cannot be uniquely defined. Any linear combination of the two degenerated vectors d_1 and d_2 which satisfy the orthogonality give equally valid vectors:

$$d_1' = d_1 \cos \varphi + d_2 \sin \varphi$$

$$d_2' = -d_1 \sin \varphi + d_2 \cos \varphi.$$

It should be mentioned that orthogonality for the degenerated vectors (in contrast to the other) is ensured by an additional procedure in the programs.

Hence, the degeneracy has the consequence that the rectangular arrangement of both vectors cannot be fixed. In our example any linear combination rotates both orthogonal vectors around φ in a plane over the benzene ring (cf. Fig. 2).

We can leave the P-SP 2 moving the proton along the symmetry plane dividing the middle of two bonds of the benzene system (procedure A using symmetry conservation: A+SC). The result is a SP 1 representing the type of transition

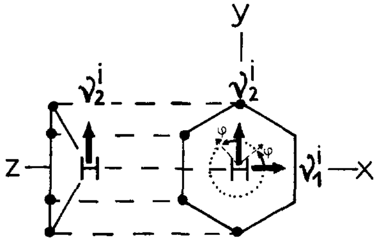
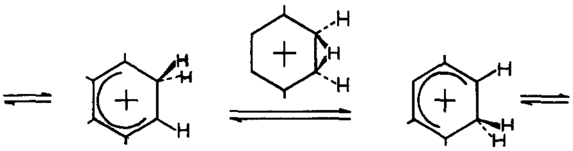


Fig. 2 Face protonated benzene: d-mode and dc-vectors, respectively, of the P-SP 2. Because of the degeneracy the vector cross cannot be fixed and is arbitrarily arranged in the figure, cf. text. With exception of the H_{1x} and H_{1y} all vector components are ≤ 0.07 (d-mode vector) and ≤ 0.015 (dc-vector)

structures of the proton shifts within the protonated benzene:

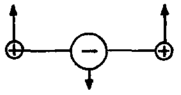


On the other hand, moving the central proton of the P-SP 2 towards a carbon atom (A or A+SC) we get one of the formulated minima (σ-complexes, the energy difference between the face structure and the minima is calculated to be $\Delta E_{pot} \approx 325$ kJ/mol). Note that the MINDO/3 barrier height of the proton shifts ($\Delta E^{\ddagger}_{pot} = 33$ kJ/mol) was shown to be theorectically significant and consistent with experimental experience (cf. [22-23]).

We conclude: face protonated aromatic compounds are high-energy saddle points of index 2 which prevent proton shifts across the ring. Therefore, the proton shifts take place at the periphery of the rings. This kind of conclusion generally characterizes the possibilities in the interpretation of chemical reactivity by appearance of P-SP 2.

Third example: structures with linear —C—O—H bonds

If more than one but the same atoms of a system are concerned in the two d-modes we have again a P-SP 2. For the linear water molecule (localized by A+SC, unstable with 122,5 kJ/mol) the degenerated imaginary frequencies are $\nu_1^i = \nu_2^i = 1593i\ \mathrm{cm}^{-1}$, representing two d-modes which may be illustrated as two orthogonal vibrations of the same type (arrows and signs, respectively; cf. the degenerated normal modes for stable linear systems like CO_2):



With no mass-weighting (dc-vector) the main atomic displacements are not given by the hydrogens but the oxygen.

Other linear —C—O—H arrangements (in alcohols etc.) also have the character of P-SP 2 without degeneracy in the d-modes. No SP 1 is produced if we follow an eigenvector which belong to one of the two directions of negative curvature (or any linear combination between the two eigenvectors) towards the next stationary point.

Finally, let us note that the two directions of the descent vectors (d-mode vectors) of a P-SP 2 in general have only a mathematical meaning and are to be identified by means of the small and the broad ridge, respectively, which result from the harmonically approximated P-SP 2. In other words, they characterize main axes orientations leading down from a hill defined over the "descent coordinates".

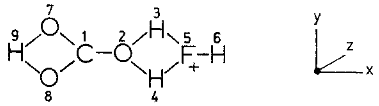
4. The "Virtual Saddle Point of Index 2" (V-SP 2)

From the P-SP 2 type we may distinguish a further type of SP 2, the so-called virtual saddle point of index 2. In this case the two d-modes do affect *different* atoms. Each d-mode has to be regarded as belonging to one of two saddle points of index 1 represented in the given structure of the system.

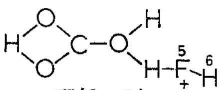
From a chemical point of view both d-modes represent in this case two transition states of relatively independent processes in the system. Such a situation has to be expected only for polyatomic systems.

Moving the system along one of the descent vectors of the V-SP 2 a next stationary point is by no means a minimum but a SP 1 (or again a V-SP 2). The d-mode of that new SP 1 (or one d-mode of the possible SP 2) is directly related to one of the original V-SP 2.

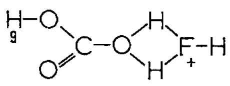
First example: $H_2CO_3 \ldots H_2F^+$ *in a twofold cyclic transfer* (*I*)



I(C_S/A+SC)



II(C_1/B)



III(C_1/B)

In structure I (optimized by A+SC) we simultaneously realized two (hypothetical) transition structures for transfer reactions. In comparing the two imaginary frequencies of I with that of the next SP 1 (structures II and III) we find the relations

$$\nu_1^i(\mathrm{I}) \triangleq \nu^i(\mathrm{II})$$

and

$$\nu_2^i(\mathrm{I}) \triangleq \nu^i(\mathrm{III})$$

as postulated above. As expected the quantiative agreement is best for large imaginary frequencies.

Table 2. Comparison of the characteristic displacement vectors of a V-SP 2 (I) with that of the two implied SP 1 (II and III); numbering cf. text, further comments see Table 1

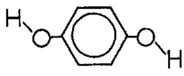
	Structure I (V-SP 2)		*Structure* II (SP 1)	
Atoms/ coordinates	dc-vector $-\lambda_1$	d-mode-vector $\nu_1^i(2613i\ \mathrm{cm}^{-1})^a$	dc-vector $-\lambda$	d-mode-vector $\nu^i(2601i\ \mathrm{cm}^{-1})$
1*y*	−0.28		−0.28	
7*x*	−0.32		−0.32	
y	−0.26		−0.26	
8*x*	0.32		0.32	
y	−0.26		−0.26	
9*y*	0.76	0.96	0.76	0.96
			Structure III (SP 1′)	
	$-\lambda_2$	$\nu_2^i(143i\ \mathrm{cm}^{-1})$	$-\lambda$	$\nu^i(136i\ \mathrm{cm}^{-1})$
2*y*	−0.22	−0.52	−0.22	−0.50
3*x*	0.29	0.21	(0.17)	(0.12)
y	−0.41	−0.28	−0.35	−0.23
4*x*	−0.29	−0.21	−0.37	−0.25
y	−0.41	−0.28	−0.43	−0.28
5*y*	0.30	0.45	0.32	0.48
6*y*	0.50	0.25	0.51	0.23
7*x*		0.29		0.27
8*x*		−0.29		−0.35

[a] The large ν_1^i (I) and ν^i (II) are necessarily related to a large energy difference $\Delta E_{\mathrm{I\text{-}III}}$ (274 kJ/mol, MINDO/3). The small ν_2^i (I) and ν^i (III) are here related to the small $\Delta E_{\mathrm{I\text{-}II}} \approx$ 13 kJ/mol

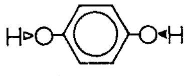
This example shows imaginary frequencies of quite different complexity concerning the displacement vectors. Especially the vectors of III give an impression of the influence of mass-weighting in comparison to the situation on the potential surface (Table 2).

To point out further characteristic V-SP 2 we chose as second example a p-substituted aromatic compound representing a degenerated case.

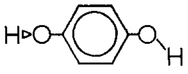
Second example: p-Hydroquinone in the out-of-plane structure IV



V(C_{2h}/A)



IV(C_{2h}/A+SC)



VI(C_1/B)

The two reaction centers in IV (here simply an overcoming of rotational barriers) are separated by the aromatic ring. Thus, the system is best qualified for the occurence of V-SP 2. Of course, the p-substituents may be of another type and different chemical reactions could be simulated allowing the construction of any number of V-SP 2.

Structure VI represents one of the neighbouring SP 1 and V one of the corresponding minima. The V-SP 2 IV cannot be identified by an analysis of the d-vectors because of the degeneracy of the two d-modes. A linear combination of two such d-vectors may produce pairs of vectors containing displacement components of both hydrogens.

An identification of the degenerated V-SP 2 may be given more intuitively by looking for two chemical processes connected with the corresponding d-modes. A more exact approach is given by removing the symmetry plane between the two centers (e.g., by small angle deformation in the reaction center one against two; the asymmetry will be not completely removed after gradient geometry optimization on the basis of a lower symmetry group). For the disturbed systems we get two slightly different d-modes with well-defined d-vectors suitable for the analysis.

A further aspect should be mentioned. In contrast to P-SP 2 each descent (d-mode) vector in a V-SP 2 characterizes the first step towards a (local) minimum energy path. Following one of the two vectors downhill we find a local minimum on one part of the surface which is relatively independent from the other part containing the SP 1 whose displacement vector is related to the second imaginary mode of the V-SP 2.

5. Conclusions

We selected two important types of saddle points of index 2: the virtual saddle point (V-SP 2) and the proper saddle point of index 2 (P-SP 2).

The V-SP 2 appears as geometrical representation of two first order saddle points in a chemical system where two independent chemical processes can be defined. The identification of a V-SP 2 leads to a simple strategy for the localization of the 2 neighbouring transition states. It is characterized by the fact that the two decomposition modes concern two *different* reaction centers (the term "reaction" is here used for all processes overcoming a barrier on a potential surface). The V-SP 2 will be found by the analysis of the eigenvectors of the decomposition modes with the exception of degenerated cases.

A P-SP 2 is characterized by the fact, that the two decomposition modes affect the same atom or atomic group. P-SP 2 are (as other stationary points) necessary for a complete topological characterization of the system. We remember the fact that a given type of structure may represent different kinds of stationary points (among them SP 2) already by substituting one atom by another one (cf. face cationized benzene, discussed in this paper). That is, P-SP 2 may characterize structures which are supposed to be of importance from chemical intuition and have thus to be considered in theoretical analysis. Independently, high lying P-SP 2 characterize "forbidden" regions for reaction paths. Together with neighbouring minima and SP 1 they give valuable information where the trajectories of a chemical reaction should mainly be concentrated. The paper also elucidates the construction of SP of a higher index by a suitable combination of two or a higher number of SP 1, SP 2, ... SP n. Of course, a spectrum of transitions exist between the two boundary cases outlined above. It should be mentioned that some properties of semiempirical methods facilitate the occurence of some type of SP 2. So it is well-known that semiempirical methods tend to destabilize symmetric in comparison to asymmetric structures [24] (cf. the sec. propyl cation) calculating plane SP 1 as SP 2 by an additional deformation mode of the skeleton.

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