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Topological complexity of potential surfaces and application to C_2H_2 molecule

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Summary. In this work, we search for the "simplest" complete surfaces of systems with three and four atoms, i.e. the minimal sets of critical points with their index, which are topologically consistent in the whole configuration space. Then we show the smallest change in the A_2B_2 system by requiring at least one stable "acetylene" configuration and one stable "vinylidene" configuration, like on the C_2H_2 surface. Finally, we give complete sets of minima, saddle points and maxima obtained for C_2H_2 with analytical potentials proposed in the literature and with a semi-empirical method at the CAS-CI level.

Key words: Potential surfaces – C_2H_2

1 Introduction

In chemistry, *ab initio* calculations and experimental data provide knowledge on certain aspects of potential surfaces: typically minima, saddle points and dissociative configurations.

However, in molecular dynamics the whole surface is required in analytical form. Therefore one builds an analytical expression fitting the previously known parts of the surface. The problem then is to control the quality of the analytical function in other huge regions.

Random checks are unsatisfactory as soon as the system exceeds three atoms, but the location of the critical points of any index n (the number of imaginary frequencies or the number of strictly negative eigenvalues of the hessian) give a powerful summary of the fitted surface. This is undertaken with the help of optimization methods: pseudo-Newton (Davidon–Fletcher–Powell or Broyden–Fletcher–Goldfarb–Shanno) [1], gradient norm minimizer [2], chain method [3, 4], and simulated annealing strategies [5]. However, the search requires criteria of completion and help to rough location of "missing" critical points. This is the crucial point where master results from algebraic topology are of decisive help.

In a preceding paper [6] whe have shown the usefulness of the Morse theory in various forms, checking topological consistency not only in symmetry-constrained cross sections but also in the whole configuration space.

The aim of the following sections is to recall the Morse inequalities linking the numbers of critical points with index n, to find the coherent "germs" of an artificial surface without and with restrictions (for example by fixing minima on the potential surface), and to give a topological analysis of potentials proposed in the literature for the C_2H_2 molecule [7–9]. Results obtained with the semi-empirical MNDOC + CAS-CI method [10] are also given.

2 The equivariant Morse inequalities

Let $V(q_1, \ldots, q_{3N})$ be the morsified function[1] of a set of N nuclei with cartesian coordinates q_i and masses μ_i. The configuration space (CS) is derived from $\mathscr{R}^{3N}$ in the following way (see [6, 11–13]):

- omission by excision of $D_{\text{excl.}}$ the set of configurations with two or more superimposed nuclei;
- elimination by mapping of the three translational degrees of freedom;
- elimination by quotient of the two or three rotational degrees of freedom.

Then CS = $M/\mathrm{SO}(3)$ with $M = \{\mathscr{R}^{3N} \backslash D_{\text{excl.}}, \sum_{i=1}^{N} \mu_i q_i = 0\}$ and where SO(3) is the rotation group in $\mathscr{R}^3$.

Introducing M_n and m_n, the numbers of critical points with index n for nonlinear and collinear configurations, respectively, the Morse theory takes the equivariant form on the whole configuration space CS:

$$\sum_{i=0}^{3N-6} M_i t^i + \frac{\sum_{j=0}^{3N-5} m_j t^j}{1-t^2} = \frac{(1+2t^2)\cdots(1+(N-1)t^2)}{1-t^2} + (1+t)Q(t), \quad (1)$$

where $Q(t)$ is a polynomial function with nonnegative coefficients.

When restricting the study of the potential function to the linear plus planar configurations, the equivariant form of the Morse theory becomes on the planar configuration space CSP:

$$2\sum_{i=0}^{2N-3} M'_i t^i + \sum_{j=0}^{2N-3} m'_j t^j = (1+2t)\ldots(1+(N-1)t) + (1+t)Q'(t). \quad (2)$$

M'_n and m'_n are the new numbers of critical points with index n for planar and collinear configurations, respectively, and $Q'(t)$ is also a polynomial function with nonnegative coefficients.

Because $Q(t)$ and $Q'(t)$ are polynomial functions with nonnegative coefficients, Eqs. (1) and (2) lead to the Morse inequalities in CS and CSP, respectively. For example, when $N = 4$, Eq. (1) leads to the following inequalities in CS:

$$M_0 + m_0 \geqslant 1$$

$$M_1 - M_0 + m_1 - m_0 \geqslant -1$$

$$M_2 - M_1 + M_0 + m_2 - m_1 + 2m_0 \geqslant 7$$

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[1] A potential function belongs to the generic class of the so-called Morse functions when it turns out to be uniformly smooth and exhibits non-degenerate critical points, i.e. no zero eigenvalues of the hessian at a critical point.

$$M_3 - M_2 + M_1 - M_0 + m_3 - m_2 + 2m_1 - 2m_0 \geqslant -7$$

$$M_4 - M_3 + M_2 - M_1 + M_0 + m_4 - m_3 + 2m_2 - 2m_1 + 3m_0 \geqslant 19$$

$$M_5 - M_4 + M_3 - M_2 + M_1 - M_0 + m_5 - m_4 + 2m_3 - 2m_2 + 3m_1 - 3m_0 \geqslant -19$$

$$M_6 - M_5 + M_4 - M_3 + M_2 - M_1 + M_0 + m_6 - m_5 + 2m_4 - 2m_3 + 3m_2 - 3m_1 + 4m_0 \geqslant 31$$

and to the equality: $(-1)^{(3N-5)} m_{3N-5} + \ldots + m_2 - m_1 + m_0 = 4!/2$.

Still for $N = 4$, Eq. (2) leads to the inequalities in CSP:

$$2M'_0 + m'_0 \geqslant 1$$

$$2M'_1 - 2M'_0 + m'_1 - m'_0 \geqslant 4$$

$$2M'_2 - 2M'_1 + 2M'_0 + m'_2 - m'_1 + m'_0 \geqslant 2$$

$$2M'_3 - 2M'_2 + 2M'_1 - 2M'_0 + m'_3 - m'_2 + m'_1 - m'_0 \geqslant -2$$

$$2M'_4 - 2M'_3 + 2M'_2 - 2M'_1 + 2M'_0 + m'_4 - m'_3 + m'_2 - m'_1 + m'_0 \geqslant 2$$

$$2M'_5 - 2M'_4 + 2M'_3 - 2M'_2 + 2M'_1 - 2M'_0 + m'_5 - m'_4 + m'_3 - m'_2 + m'_1 - m'_0 = -2$$

The right members of the inequalities depend on the value of N and are obtained with the help of Eqs. (1) and (2).

More, there are $N!/2$ linear configuration subspaces CSL for which Morse inequalities are

$$m''_k - m''_{k-1} + \cdots + (-1)^k m''_0 \geqslant (-1)^k.$$

The equality holds for $k = N - 1$.

3 The simplest surfaces for three and four atoms systems

From the last inequality of Sect. 2, we saw that the Morse theory predicts at least one critical point in each of the $N!/2$ linear configuration spaces CSL ($m''_0 \geqslant 1$), these subspaces being separated by high energy barriers corresponding to configurations with superimposed atoms. Then if all the atoms are different, there are at least $N!/2$ $C_{\infty v}$ critical points in the whole configuration space CS and CSP. More, the bending modes of all these critical points lead to planar configurations belonging to the C_s-subgroup included in the $C_{\infty v}$-group, so that the simplest surface could be described by the only set of linear $C_{\infty v}$ critical points. Effectively, the equivariant Morse theory can be checked in this case provided that one has a good set of linear critical points with 0, 1, 2, ... unstable bending modes (see ABC and ABCD in Table 1). In fact this set must correspond to the coefficients of the Poincaré polynomial function $(1 + 2t) \ldots (1 + (N - 1)t)$ given in Eq. (2), also called the Betti numbers: (1, 2) for $N = 3$ and (1, 5, 6) for $N = 4$.

When several atoms are equivalent, some of the $N!/2$ critical points are equivalent (by permutation of equivalent atoms) and can be put together: for example, there are two $C_{\infty v}$-configurations (AABB and ABAB) and two $D_{\infty h}$-configurations (ABBA and BAAB) including in fact 4 and 2 equivalent critical points, respectively (4 and 2 are the symmetry numbers of the $C_{\infty v}$ and $D_{\infty h}$ critical

Table 1. Simplest surfaces for three and four atoms systems

Molecule	Label	Symmetry number		Index		Unstable modes
			CS	CSP	CSL	
ABC						
	$C_{\infty v}$	1	0	0	0	
	$2C_{\infty v}$	1	2	1	0	Π
AB_2						
	$D_{\infty h}$	1	0	0	0	
	$C_{\infty v}$	2	2	1	0	Π
A_3						
	$D_{\infty h}$	3	2	1	0	Π_u
	D_{3h}	1	0	0		
ABCD						
	$C_{\infty v}$	1	0	0	0	
	$5C_{\infty v}$	1	2	1	0	Π
	$6C_{\infty v}$	1	4	2	0	2Π
ABC_2						
	$3C_{\infty v}$	2	2	1	0	Π
	$3C_{\infty v}$	2	4	2	0	2Π
	C_{2v}	1	0	0		
AB_3						
	$C_{\infty v}$	6	2	1	0	Π
	$C_{\infty v}$	6	4	2	0	2Π
	D_{3h}	1	0	0		
A_2B_2						
	$D_{\infty h}$	2	0	0	0	
	$D_{\infty h}$	2	4	2	0	Π_g, Π_u
	$C_{\infty v}$	4	2	1	0	Π
	$C_{\infty v}$	4	4	2	0	2Π
	D_{2h}	1	1	1		B_{1g}
A_4						
	$D_{\infty h}$	12	2	1	0	Π_g
	D_{4h}	3	3	2		B_{2u}, E_u
	D_{3h}	4	1	0		A_2''
	T_d	2	0			

points, respectively, for A_2B_2 and given in Table 1). The smallest number of linear critical points is still equal to $4!/2$ ($= 4 + 4 + 2 + 2$) but the equivariant Morse inequalities are no longer satisfied in CSP (nor in CS) because we can no more have one minimum, five saddle points and six maxima with this set of twelve linear critical points. Planar or spatial critical points appear necessary. The sole non-linear symmetry group including other subgroups (kernels [14]) and not included in the linear ones is D_{2h}. Effectively D_{2h} includes: $\{C_{2h}, C_{2v}^{(2,4,2)A}, C_{2v}^{(2,4,2)B}, C_{2v}^{(0,2,2)}\}$ and then $\{C_s^{(4)}, C_2, C_s^{(2)A}, C_s^{(2)B}, C_1\}$[2], that is all the non-linear symmetry groups of

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[2] The exponents of the C_{2v} groups mean how many atoms are respectively on the C_2 axis (A or B) and in the σ_v and σ_d planes; for C_s groups, the exponents mean how many A or B atoms are in σ_h plane.

A_2B_2 except $C_{2v}^{(0,4,0)}$ which is a kernel of $D_{\infty h}$. Then the D_{2h} cross section must own one minimum at least and this minimum remains a critical point with possibly different indices in lower symmetry cross sections like C_{2h} (which owns also $D_{\infty h}$ configurations) and in CS or CSP.

A set of the compulsory present high symmetry critical points ($2D_{\infty h}$, $2C_{\infty v}$ and $1D_{2h}$ for A_2B_2) can be sufficient to check equivariant Morse inequalities: no more critical points with a lower symmetry are necessary. In that way we report in Table 1 the simplest surfaces for three and four atom systems. However, unstable modes have been obtained in checking the Morse theory in each cross section.

Let us develop the A_2B_2 example with the help of Table 1.

1. In the linear ABBA, BAAB, AABB, ad ABAB configuration spaces, there is one minimum in each cross section (CSL indices are zeros for both $D_{\infty h}$ and both $C_{\infty v}$ critical points).

2. In the planar configuration space CSP:

– one of the two $D_{\infty h}$ critical points with symmetry number 2 is a minimum: $m'_0 = 2$;
– one of the two $C_{\infty v}$ critical points with symmetry number 4 is a saddle point: $m'_1 = 4$;
– the other $D_{\infty h}$ and $C_{\infty v}$ critical points are maxima: $m'_2 = 2 + 4$;
– the D_{2h} critical point with symmetry number 1 is a saddle point: $M'_1 = 1$ and there is no more critical point: $M'_0 = M'_2 = 0$.

Then, we have

$$2M'_0 + m'_0 = 2 \geqslant 1,$$

$$2M'_1 - 2M'_0 + m'_1 - m'_0 = 4 \geqslant 4,$$

$$2M'_2 - 2M'_1 + 2M'_0 + m'_2 - m'_1 + m'_0 = 2.$$

The third inequality is already an equality and all the equivariant inequalities in CSP are checked.

3. In the spatial configuration space: $m_0 = 2$, $m_2 = 4$, $m_4 = 2 + 4$, $M_0 = 0$, $M_1 = 1$, $M_2 = 0$. Because the molecule is stable in the plane, the planar critical point has the same indice in the spatial and planar configuration spaces; more, there is no spatial critical points. Equivariant inequalities in CS are also checked:

$$M_0 + m_0 = 2 \geqslant 1,$$

$$M_1 - M_0 + m_1 - m_0 = -1 \geqslant -1,$$

$$M_2 - M_1 + M_0 + m_2 - m_1 + 2m_0 = 7 \geqslant 7,$$

$$M_3 - M_2 + M_1 - M_0 + m_3 - m_2 + 2m_1 - 2m_0 = -7 \geqslant -7,$$

$$M_4 - M_3 + M_2 - M_1 + m_4 - m_3 + 2m_2 - 2m_1 + 3m_0 = 19 \geqslant 19$$

and

$$-m_7 + m_6 - m_5 + m_4 - m_3 + m_2 - m_1 + m_0 = 12 = 4!/2.$$

Unstable modes of each critical point given in Table 1 allow to check the usual Morse inequalities in every cross sections.

Still in the case of A_2B_2 (Table 1), it is also interesting to extend the "manifold with boundary" approach proposed for three-body systems by P. G. Mezey [15]. In order to avoid reflexion properties for four-body systems, the sets of collinear

Table 2. Simplest surface for C_2H_2 with the stable acetylene and vinylidene critical points

Molecule	Label	Symmetry number	Index CS	 CSP	 CSL	Unstable modes
C_2H_2						
Acetylene	$D_{\infty h}$	2	0	0	0	
	$D_{\infty h}$	2	4	2	0	Π_g, Π_u
	$C_{\infty v}$	4	2	1	0	Π
	$C_{\infty v}$	4	4	2	0	2Π
	D_{2h}	1	2	2		B_{1g}, B_{2u}
Vinylidene	$C_{2v}^{(242)C}$	2	0	0		
	$C_s^{(4)}$	4	1	1		A'

and now planar configurations have to belong to the boundary; the Betti numbers are those of a ball S^6 (1, 0, 0, 0, 0, 0, 1) when all the linear critical points unstable in the bending mode and all the planar critical points unstable in the spatial mode are bound in one artificial maximum point (see Appendix 2 in [6]). The last inequality becomes an equality and is a more restrictive condition than spatial equivariant inequalities; however several critical points must not be taken into account and a chemical information is lost. With the help of Table 1 (A_2B_2), where one $D_{\infty h}$ and two $C_{\infty v}$ critical points unstable in a bending mode have to be excluded and where the symmetry numbers remain unchanged for linear and planar configurations, we find:

$$\begin{aligned} M_0'' &= 2 \geqslant 1, \\ M_1'' - M_0'' &= -1 \geqslant -1, \\ M_2'' - M_1'' + M_0'' &= 1 \geqslant 1, \\ &\vdots \end{aligned}$$

and with the artificial maximum point, we have

$$M_6'' - \cdots + M_0'' = 2\ (= 1 + (-1)^6).$$

4 Application to C_2H_2

Improvements in experimental techniques have led recently to progress in the understanding of the nature of vibrational energy flow in highly excited polyatomic molecules; in particular the experimental spectrum of highly excited ground state acetylene has been obtained (see [9] and references therein). More C_2H_2 is a A_2B_2 system which has been already studied at the *ab initio* level, in [16–19] for example.

We know that the vinylidene configuration ($C_{2v}^{(242)C}$) is a minimum on the potential surface. In Table 2, we give the topological features of the simplest C_2H_2 surface taking this fact into account. Of course, the appearance of a new minimum (vinylidene) also implies the appearance of a saddle point, $C_s^{(4)}$, to connect with the other minimum (acetylene). But also the D_{2h} critical point is no longer a minimum in the $C_{2v}^{(242)C}$ cross section and becomes a critical point of index 2 in the configuration space. This point illustrates what Morse theory affords: chemistry

Table 3a–c. Critical points of the whole CMM analytical potential function (the origin of the energy corresponds to the dissociated system). m_1, m_2, m_3, s_1 and s_2 are the three minima and two saddle points represented in Fig. 3

Label	Energy	Symmetry		Index		Unstable modes
	(kcal/mol)	number	CS	CSP	CSL	
Linear						
$D_{\infty h}$						
Acetylene	−404.8478	2	0	0	0	
CHHC	−238.1648	2	4	2	0	Π_g, Π_u
$C_{\infty v}$						
CHCH	−312.1767	4	2	1	0	Π
CCHH	−298.9441	4	0	0	0	
	−264.6077	4	0	0	0	
	−261.9563	4	1	1	1	Σ^+

Table 3b.

Label	Energy	Symmetry		Index		Unstable modes
	(kcal/mol)	number	CS	CSP	CSL	
Planar						
D_{2h}						
m_1	−342.2089	1	1	1		B_{1g}
m_2	−303.6921	1	2	2		B_{1g}, B_{2u}
s_1	−282.0277	1	3	3		A_g, B_{1g}, B_{2u}
m_3	−239.0487	1	2	2		B_{1g}, B_{2u}
s_2	−234.2989	1	3	3		A_g, B_{1g}, B_{2u}
	−117.2050	1	3	2		B_{1g}, B_{1u}, B_{3u}
	−103.9763	1	4	3		$A_g, B_{1g}, B_{1u}, B_{3u}$
C_{2h}						
	−304.2629	2	1	1		B_u
	−303.6971	2	2	2		A_g, B_u
	−293.0016	2	1	1		B_u
	−263.0329	2	3	2		A_g, A_u, B_u
$C_{2v}^{(0,4,0)}$						
	−268.4595	2	2	1		A_2, B_1
	−266.7693	2	3	2		A_1, A_2, B_1
	−259.5780	2	1	1		B_1
	−235.9114	2	2	2		A_1, B_1
	−125.2052	2	1	1		B_1
	−125.1769	2	2	2		A_1, B_1
	−124.5527	2	2	2		A_1, B_1
	−118.9852	2	3	3		$2A_1, B_1$
$C_{2v}^{(2,4,2)C}$						
Vinylidene	−364.7715	2	0	0		
	−318.8679	2	2	2		A_1, B_1
	−300.6937	2	1	1		B_1
	−282.0684	2	2	1		A_1, B_2
	−259.1257	2	1	1		B_1
	−228.6220	2	2	2		A_1, B_1

Table 3b. (contd.)

Label	Energy	Symmetry		Index		Unstable modes
	(kcal/mol)	number	CS	CSP	CSL	
$C_{2v}^{(2,4,2)H}$						
	−279.2071	2	0	0		
	−264.5826	2	0	0		
	−259.5644	2	3	2		A_1, B_1, B_2
	−259.0118	2	2	1		B_1, B_2
	−258.8738	2	1	1		A_1
	−164.7697	2	2	2		A_1, B_1
$C_s^{(4)}$						
	−323.6922	4	0	0		
	−297.3807	4	1	1		A'
	−291.9649	4	1	1		A'
	−281.9596	4	3	2		$2A', A''$
	−278.7357	4	1	1		A'
	−277.3772	4	1	1		A'
	−275.5633	4	2	2		$2A'$
	−263.6917	4	1	1		A'
	−258.6560	4	2	2		$2A'$
	−258.2498	4	2	2		$2A'$
	−227.4199	4	3	3		$3A'$

Table 3c.

Label	Energy	Symmetry		Index		Unstable modes
	(kcal/mol)	number	CS	CSP	CSL	
Spatial						
$C_{2v}^{(0,2,2)}$						
	−259.2044	2	2			B_1, B_2
	−228.4728	2	3			A_1, A_2, B_2
	−110.2010	2	3			A_1, B_1, B_2
	−106.6664	2	4			$2A_1, A_2, B_2$
C_2						
	−266.7948	4	2			A, B
$C_s^{(2)H}$						
	−277.5606	4	1			A''
	−277.3712	4	2			A', A''
	−273.7274	4	3			$A', 2A''$
	−164.4762	4	3			$2A', A''$
$C_s^{(2)C}$						
	−289.9805	4	1			A'
	−258.5919	4	2			A', A''
	−226.4149	4	4			$2A', 2A''$
C_1						
	−288.6051	8	2			$2A$
	−275.3240	8	3			$3A$

Table 4. Numbers n/m of critical points for each index value in the spatial/planar configuration spaces and for different energy bands (permutation of equivalent atoms are not taken into account)

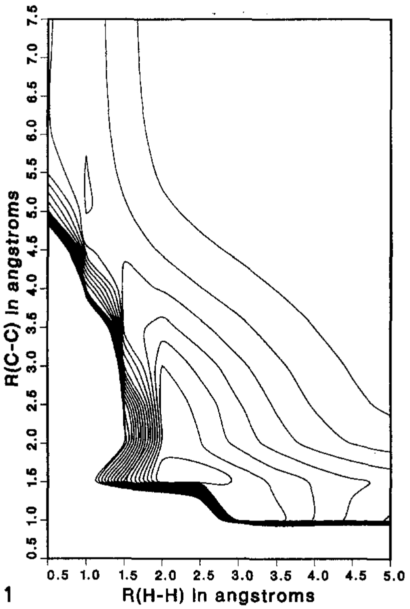
Energy/Index	0	1	2	3	4	5	6
−100							
	0/0	1/1	2/3	3/2	2/0	0/0	0/0
−150							
	0/0	0/0	1/1	1/0	0/0	0/0	0/0
−200							
	0/0	0/0	3/4	3/2	2/0	0/0	0/0
−250							
	4/4	12/13	11/7	7/1	0/0	0/0	0/0
−300							
	1/1	3/4	4/3	0/0	0/0	0/0	0/0
−350							
	1/1	0/0	0/0	0/0	0/0	0/0	0/0
−400							
	1/1	0/0	0/0	0/0	0/0	0/0	0/0

introduces a local perturbation (a new minimum) and Morse theory gives the global answers of the potential surface. We just selected in Table 2 the simplest answer according to a principle of least complexity.

In this point, we studied three analytical potentials for C_2H_2 given in the literature. The potential functions are eventually Morsified by adding a long-range penalty function which converts repulsive valleys and ridges onto ordinary critical points (see [6], Appendix 1) and all the inequalities of Sect. 2 linking the critical points must be checked for $N = 4$.

We first search for minima belonging to high-symmetry cross sections like $D_{\infty h}$ or D_{2h} with pseudo-Newton methods (see [1, 2]), and saddle points between themselves with the "chain" method [3, 4]; then we release gradually symmetry constraints while checking usual Morse inequalities, the configuration subspaces being balls $\mathcal{R}^n$ and torus $\mathcal{T}^n$ with Betti numbers $(1, 0, \dots, 0)$ and $(C_n^0, C_n^1, \dots, C_n^n)$, respectively. In the absence of strong symmetry constraints like in CSP and CS (i.e. for $C_s^{(4)}$ and C_1 configurations), we use simulated annealing strategies [5] on the potential V or its gradient, in order to find not only missing minima but also any kind of critical points, until the equivariant Morse inequalities are satisfied as well as the Morse inequalities in the "manifold with boundary" proposed by Mezey [6, 15].

The critical points found for the analytical potential proposed by Carter and coll. (CMM) [7] are summarized in Table 3. We retrieve the vinylidene and acetylene minima and also three of the four linear critical points of Table 2 with the same indices: two $D_{\infty h}$ critical points with indices 0 and 4, and one $C_{\infty v}$ with index 2 in CS. On the contrary, even if the three CCHH critical points can be collapsed in only one minimum (two minima separated by a saddle point), the index 0 is far from the expected one 4, given in Table 2. The number of critical points becomes also very large (62 including 7 D_{2h}, 11 $C_s^{(4)}$, etc.) and 14 spatial critical points appear. The energy distribution of the critical points given in Table 4 for the CMM analytical potential is much higher than the energy of the few well known chemical configurations; this is probably due to the polynomial form of the potential function responsible for a large number of pre-dissociated configurations.



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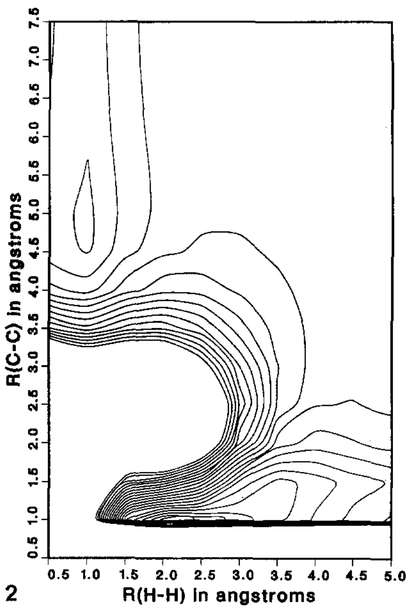

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Fig. 1. D_{2h} cross section of the CMM potential function

Fig. 2. D_{2h} cross section of the HCC potential function

This large number of critical points is also found with another analytical potential (HCC) [8], based on a similar polynomial approach. Figures 1 and 2 give the iso-energy lines (from -300 to $+600$ kcal/mol) obtained from CMM and HCC potential functions in the D_{2h} cross section. Comparatively to Fig. 1, we guess in Fig. 2 one more maximum and then one more saddle point, very high in energy, pushing out the other more realistic saddle point. Figure 3 is a zoom of Figure 1 around its lowest minimum: three minima and two saddle points appear. There are actually seven critical points in D_{2h} cross section (see Table 3b), very close in geometries, but not at all in energies. This set of seven critical points could formally be contracted to a single minimum in the cross section, e.g. at energy -342.2089 kcal/mol, and with index 1 (B_{1g}) in the whole configuration space. The other D_{2h} critical points are pairs different in the stability of only one mode A_g of the group D_{2h} and then cancel themselves by the contraction procedure [20].

The third potential studied (HL) [9] proceeds from a radically different analytical approach. The authors claim the advantages of a small number of "smooth" (almost monotonous) functions to avoid spurious high-energy features. Actually very few critical points are generated. Unfortunately, the HL potential still exhibits several deficiencies, at least from the topological standpoint. For example, the superimposition of C and H atoms is not forbidden and the four kinds of linear species are not always separated by high-energy barriers! Only two linear configurations are obtained: HCCH (acetylene, index 0) and CCHH (index 2). More the dissociative channel C_2H + H corresponds to a critical orbit (a dense set of critical points) because the potential becomes insensitive to the CCH angle in this case. Therefore, not only the Morse theory cannot be checked but also the model is

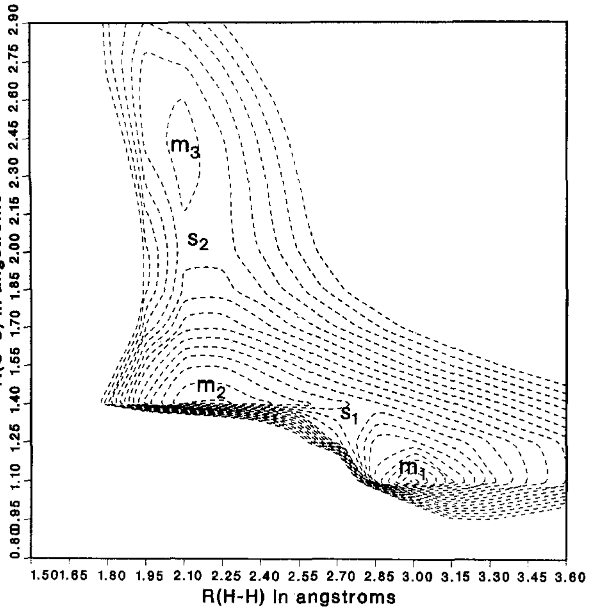

Fig. 3. Zoom of the CMM D_{2h} cross section: five of the seven critical points are represented (see Table 3b)

unsuitable for molecular dynamics at the approach of the lowest dissociative channel. Discarding these defects, the potential surface is close to the simplest surface including the vinylidene as a minimum (Table 2). However the out-of-plane mode of the D_{2h} critical point is unstable (index equal to 3 instead of 2). This implies the emergence of a non-planar $C_{2v}^{(0,2,2)}$ critical point with index two.

Standard (i.e. SCF closed shell) semi-empirical calculations (MNDOC) give the same set of critical points and indices than the HL potential and restore the "missing" linear critical points CHCH and CHHC (although poorly described energetically as closed shell species). This rough agreement indicates that it could be the topology of the genuine potential for C_2H_2. However, the $C_{2v}^{(0,2,2)}$ critical point is not a minimum as found by *ab initio* including *d*-orbital [17]. Also the MNDO heat of reaction and energy barrier to isomerization process acetylene (0. kcal/mol) $\leftrightarrow C_s^{(4)}$ (94.11 kcal/mol) $\leftrightarrow$ vinylidene (63.78 kcal/mol) are poor with respect to a decisive *ab initio* approach [16]. In spite of the absence of *d*-orbitals, semi-empirical energies become fairly acceptable at the MNDO-CI level involving up to the 10 molecular orbitals of the valence shell[3]. Moreover, the $C_{2v}^{(0,2,2)}$ critical point becomes a minimum in accordance with *ab initio* [17]. According to Morse theory, this implies the emergence of other critical points, not searched for in [17]. Three other critical points are found on the MNDO-CI surface: C_2 and $C_s^{(2)C}$ saddle points toward acetylene and vinylidene respectively, and a C_1 critical point of index 2. However, they are so close in energy and geometry that they can

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[3] The molecular orbitals come from a moderately polarized SCF scheme involving a large number of open shells. About 80 microstates are then extracted from the 63504 ones generated by the CAS-CI. The selection refers to a small set of representative microstates and enlarges it by a perturbation technique. This procedure pick out most of the specific effects of a CI and avoid an overestimate of the correlation energy. Method implemented as a standard in the AMPAC 5.0 package [10b].

Table 5. MNDO-CI critical points. X is the midpoint of the C–C bond, $\theta_i = H_i\hat{X}C_1$ and ϕ the dihedral angle. In parentheses: *ab initio* results for the singlet state [17] (energy with zero-point corrections)

C_2H_2	Energy kcal/mol	CS	Index CSP	CSL	X–C Å	X–H₁ Å	θ_1 deg.	X–H₂ Å	θ_2 deg.	ϕ deg.
Linear										
Acetylene										0.
	(0.)	(0)	(0)	(0)	(0.593)	(1.650)	(0.)	(1.650)	(180.)	(0.)
CCHH	140.63	4	2	0	0.5863	1.5841	0.	2.5726	0.	0.
CHCH	210.28	2	1	0	3.0919	1.9942	0.	4.1954	180.	0.
CHHC	218.22	4	2	0	3.3243	2.2245	0.	2.2245	180.	0.
Planar										
Vinylidene	43.21	0	0		0.6585	1.5512	35.9	1.5512	324.1	0.
	(39.6)	(0)	(0)		(0.647)	(1.510)	(38.2)	(1.510)	(321.8)	(0.)
$C_s^{(4)}$	69.37	1	1		0.6348	1.1694	87.1	1.6971	185.5	0.
D_{2h}	174.89	3	2		0.6525	1.1526	90.	1.1526	270.	0.
	(107.1)	(2)	(1)		(0.649)	(1.004)	(90.)	(1.004)	(270.)	(0.)
Spatial										
$C_{2v}^{(0,2,2)}$	135.06	0			0.6769	1.1603	90.	1.1603	90.	103.18
	(72.1)	(0)			(0.643)	(1.097)	(90.)	(1.097)	(90.)	(99.8)
$C_s^{(2)C}$	135.08	1			0.6773	1.1595	91.98	1.1595	91.98	103.57
C_2	135.11	1			0.6784	1.1572	87.76	1.1572	92.24	103.84
C_1	135.12	2			0.6783	1.1549	88.80	1.1598	93.17	103.88

be contracted in a single $C_{2v}^{(0,2,2)}$ critical point with an index equal to two like in the MNDOC calculations. This cluster of critical points sounds doubtful to common sense. Should *d*-orbitals be a necessity is an open question at this stage. MNDO-CI results and those of reference [17] for the singlet state (see also [16, 18, 19]) are collected in Table 5. Energies are in reasonable agreement with regards to the wanderings of analytical potentials at high energies. The only topological disagreement concerns the B_{1g} mode of the D_{2h} critical point. Topological consistency implies the existence of a C_{2h} singlet critical point on the *ab initio* surface (the C_{2h} triplet found in [17] cannot be an outgoing saddle point for the D_{2h} structure and does not belong to the ground state potential). Under this hypothesis, the *ab initio* surface should be a little more complex than the MNDO-CI one.

The open question of the topology in the large of the singlet ground state of C_2H_2 has recently been investigated at a reasonably good *ab initio* level [21]. Results indicate that a C_{2h} singlet critical point with index 3 does exist (the D_{2h} has an index equal to 2), as topologically deduced from the early study of Binkley [17]. A cluster of critical points is also found in the $C_{2v}^{(0,2,2)}$ region, as observed at the MNDO-CI level. This point incidently signifies that *d*-orbitals are not basically required for a semi-empirical study of this potential surface, in opposite to *ab initio* approaches where they act strongly as polarization functions. Adding the three other linear critical points to the set of critical points found by Halvick and coll. [21], we obtain a surface of C_2H_2 satisfying the planar and spatial equivariant Morse theory: all the inequalities of Sect. 2 are verified for $N = 4$.

At end, the genuine topology of the singlet ground state of C_2H_2 could stand at a medium level of complexity: more than the simplest one (Table 2), more than the oversmoothed HL analytical approach, but much less than the CMM or HCC ones.

5 Conclusion

This work introduces the concept of topological complexity of a potential surface in term of its number of critical points. The basic mathematical tool is the Morse theory applied to potential functions in chemistry. Either "standard" or "equivariant" forms of the Morse theory are used, depending on the part of the potential under study (from numerous symmetry-constrained cross sections to the whole configuration space). We illustrate how such general theorems, apparently far away from "normal" problems in chemistry, do interfere strongly in the numerical approaches to potential surfaces (semi-empirical, *ab initio* and analytical fits).

Following a principle of least complexity, we first derive what should be the simplest potential surfaces for general molecules with three and four atoms and it could be done also for molecules with more than four atoms. Such hypothetical surfaces play the role of germs for actual surfaces. Then we show that the introduction of a new local property (the existence of a critical point with a known index) has global consequences. Hence again these consequences may be predicted and classified on the basis of a criterion of topological complexity. This provides a decisive help either to drive further on a numerical prospection or to check the plausibility of an analytical fit.

The case of the singlet ground state of C_2H_2 is taken as an example of current interest. Three typical analytical potentials previously proposed in the literature are analysed (and criticized) on non intuitive topological grounds. Semi-empirical and *ab initio* surfaces are prospected in turn, up to topological completion. Finally we surround the main topological features spanning these later approaches. This topological framework gives the unavoidable skeleton of any kind of analytical fit to be attempted in the future.

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