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Topology of potential hypersurfaces of two, three and four dipoles interacting at long distances

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The whole sets of critical points of analytical functions corresponding to the long-range two-body interaction between two, three and four dipole vectors set at the vertices of several polygons are determined using topology theorems. Betti numbers associated to the configuration spaces are first obtained, then stationary points are located via an analytical gradient method till the Morse inequalities are checked.

1. Introduction

Theoretical study of intermolecular systems has been growing in recent years [1,2,4,7,9,14,16], a good knowledge of molecule interactions being of fundamental importance to understand quantum tunneling dynamics that occur in hydrogen-bonded systems, hydration of biochemical systems or properties in crystals, for example.

For van der Waals systems, the intermolecular surfaces are very flat and the whole set of minima and transition states is necessary to understand molecular rearrangements. The search for these numerous stationary points is a not trivial task; fortunately, the Morse theory provides a powerful framework for rationalization of numerical results [5,8,10]. In preceding works [6,12,13], we stressed the topology of the whole potential function of $3N$ coordinates for molecules or clusters with a small number N of atoms. We found that highly symmetric configurations ($D_{\infty h}, D_{3h}, D_{4h}, T_d, \ldots$) were compulsorily present on these hypersurfaces. In this work, atoms are fixed at the vertices of these crucial polygons and they are replaced by dipoles describing identical molecular fragments of a supersystem like $(CO)_N$. Inter-dipole distances are supposed to be large and rigid so that only the direction (θ_i, ϕ_i) of each dipole vector subtending a spherical space can vary. This supposes that we study the configuration (θ_i, ϕ_i)-space at the minimum of the electronic potential surface with respect to the hyper-radius of the supersystem and that each dipole takes directions set by the dipole–dipole van der Waals interaction.

The sets of Betti numbers corresponding to such topological spaces are given in section 2. Applications on two, three and four dipoles are studied in section 3.

2. Morse inequalities

Let (θ_i, ϕ_i) be the spherical coordinates corresponding to the direction of one dipole vector $\vec{d_i}$. The topological space subtended by these coordinates is the sphere $\mathcal{S}^2$ with Poincaré polynomial series $(1 + t^2)$ yielding the well-known Betti numbers (1,0,1) [3,15]. For N vectors, the whole configuration space is a space product of N spherical spaces $\mathcal{S}^2$. The Betti numbers are determined via either the Kunneth's formula [3,15] or from the coefficients of the series $(1 + t^2)^N$. For a Morse function with M_n the number of critical points C_n whith index n (the number of negative eigenvalues of the Hessian matrix), we can write

$$\sum_{n=0}^{2N} M_n t^n = \left(1 + t^2\right)^N + (1 + t)Q(t), \tag{1}$$

where $Q(t)$ is a polynomial function with non-negative coefficients. This equation leads to the Morse inequalities with a final equality for $n = 2N$.

However, when the interacting dipoles (or vectors) have their fixed origins in a straight line D, the potential function becomes invariant with respect to any rotation around D. The potential is no longer a Morse function as the critical "points" belong to actual critical orbits. The configuration space of interest becomes the quotient of S^{2N} by the rotation group *SO*(1). The space $S^{2N}/SO(1)$ fails to be a manifold, the action of the rotation on S^{2N} being not free at those configurations for which the N vectors are all collinear to D. Basic Morse theory applies onto manifolds only ([10, chapter V]), however the equivariant version of the Morse theory holds [11] and equation (1) is replaced with

$$\sum_{n=0}^{2N} M_n t^n + \sum_{n=0}^{2N} \frac{m_n t^n}{1 - t^2} = \frac{(1 + t^2)^N}{1 - t^2} + (1 + t)Q(t), \tag{2}$$

where m_n is the number of these linear configurations, and where $1/(1 - t^2)$ arises from the action of *SO*(1).

In the following, the equivalent geometric configurations for a critical point $(\theta_1, \phi_1, \ldots, \theta_N, \phi_N)$ must be enumerated to evaluate M_n (and m_n). The N origins of the vectors being fixed, the maximum number of equivalent critical points when permuting and changing the sign of the dipoles, is equal to two times the number of symmetry operators in the group formed by their connections. This result is to be divided by the number of inactive symmetry operators on the whole set of N vectors to within the global sign. For example in a D_{3h} symmetry group, a maximum of 24 (2×12) equivalent critical points can be found. But the whole set of vectors belonging also to a symmetry group, we have to divide 24 by the corresponding number of symmetry operators: in the case of critical points for which all the vectors are orthogonal to the D_{3h} plane, this number is 12 $(E, 2C_3, 3C_2, \sigma_h, 2S_3, 3\sigma_v)$ if the three vectors at the triangle vertices are in phase, or 4 $(E, C_2, \sigma_h, \sigma_v)$ for opposite phases. This ends on a number of equivalent configurations equal to 2 and 6, respectively. For "collinear"

configurations where the vector connections are aligned, this rule holds by using an abelian subgroup of $D_{\infty h}$ (e.g., D_{2h}).

A locus of interest in the configuration space is the ensemble of the "planar configurations" where the dipole connections lie in a plane and each dipole belongs to the same plane. This locus is a symmetry cross-section of the configuration space (ponctual group C_s), spanned by the ϕ_i-coordinates only ($\theta_i = \pm\pi/2$) by choosing z-axis perpendicular to the C_s plane. The homology of this cross-section is a product of one-dimensional $\mathcal{S}^1$ spheres, therefore Morse inequalities for planar configurations are obtained from the following relationship:

$$\sum_{n=0}^{N} M'_n t^n = (1+t)^N + (1+t)Q(t). \tag{3}$$

Equation (3) is not part of equation (1) or (2). The corresponding set of Morse inequalities is also of interest to check the topological consistency of numerical results.

3. Application to the dipole–dipole interaction potential

(θ_i, ϕ_i) and (θ_j, ϕ_j) being spherical angles describing the orientation of two dipoles $\vec{d_i}$ and $\vec{d_j}$ separated by a distance R_{ij} in a given orthogonal reference frame, the dipole–dipole interaction $V(i,j)$ between them reads

$$V(i,j) = \frac{-2\cos\alpha_{ij}\cos\beta_{ij} + \sin\alpha_{ij}\sin\beta_{ij}\cos\gamma_{ij}}{R_{ij}^3}, \tag{4}$$

where α_{ij} (β_{ij}) is the angle between $\vec{d_i}$ ($\vec{d_j}$) and the connection vector $\vec{R}_{ij}$, and where γ_{ij} is the dihedral angle $(\vec{d_i}, \vec{R}_{ij}, \vec{d_j})$.

For additive two-body long-range potentials, the total energy $V(\theta_1, \phi_1, \ldots, \theta_N, \phi_N)$ is equal to the sum $\sum_{i>j} V(i,j)$.

This potential function turns out to be smooth everywhere. As a consequence, the Morse theory holds provided that the function does not exhibit degenerate critical values (critical points with at least one Hessian eigenvalue equal to zero).

The potential function V, its gradient and the Hessian matrix have been obtained analytically by the formal calculation software *Mathematica* [17]. The stationary points were found by a pseudo-Newton gradient method starting from numerous trial guess, and the index of the Hessian has been collected systematically.

3.1. Interaction between two dipoles

Only four critical points summarize this trivial potential function:

– two critical points correspond to parallel and antiparallel dipoles, themselves perpendicular to the straight line D (chosen as z-axis) connecting their origin. The corresponding energies are equal to $+1$ and -1 (hartree) for an inter-dipole R

distance equal to 1 (bohr). In the two-dimensional (θ_1, θ_2)-space ($\phi_1 = \phi_2 = 0$, for example), their indices are both equal to 1 and the number of equivalent configurations is 2 for each of them, the rotation around D being forbidden. In the four-dimensional $(\theta_1, \theta_2, \phi_1, \phi_2)$-space divided by the *SO*(1) group, their indices are equal to 2 (parallel dipoles) and 1 (anti-parallel dipoles) and their symmetry number is 1 (instead of 2);

– the two other critical points correspond to dipoles parallel to D. The associated energies are -2 and $+2$ depending on whether the vectors are parallel or anti-parallel. In the two-dimensional (θ_1, θ_2)-space, their indices are 0 and 2, respectively, while they are twice larger (then equal to 0 and 4) in the whole configuration space because of the twofold degeneracy of the curvatures in the direction perpendicular to D. In both spaces, their symmetry number is equal to 2.

Collecting, we have

$M'_0 = 2,\ M'_1 = 2 + 2,\ M'_2 = 2$ in the two-dimensional space,
$M_0 = 0,\ M_1 = 1,\ M_2 = 1,\ M_3 = 0,\ M_4 = 0,\ m_0 = 2,\ m_1 = 0,\ m_2 = 0,$
$m_3 = 0$ and $m_4 = 2$ in the whole configuration space,

in full agreement with equations (3) and (2) for $N = 2$ (in the present case, the connections of the dipoles are aligned and equation (1) cannot be used).

3.2. *Interaction between three dipoles*

In a previous work [12], we have introduced a measure of "complexity" of a potential function in terms of the number of critical points exceeding the smallest number consistent with the Morse inequalities and the symmetry (in a non-rigid sense) of the problem. The "simplest" potential function for a cluster A_3 of three equivalent atoms A do have only two critical points, one with the symmetry $D_{\infty h}$ the other with the symmetry D_{3h}. In the present study, each atom A in both $D_{\infty h}$ and D_{3h} configurations is replaced with a dipole vector, the inter-dipole distances being kept constant. The orientations of the three dipoles are free and the main properties of the potential function are summarized by its critical points.

$D_{\infty h}$: from equation (2) with $N = 3$, the Morse inequalities are

$$
\begin{aligned}
M_0 + m_0 &\geqslant 1,\\
M_1 - M_0 + m_1 - m_0 &\geqslant -1,\\
M_2 - M_1 + M_0 + m_2 - m_1 + 2m_0 &\geqslant 5,\\
M_3 - M_2 + M_1 - M_0 + m_3 - m_2 + 2m_1 - 2m_0 &\geqslant -5,\\
M_4 - M_3 + M_2 - M_1 + M_0 + m_4 - m_3 + 2m_2 - 2m_1 + 3m_0 &\geqslant 12,\\
M_5 - M_4 + M_3 - M_2 + M_1 - M_0 + m_5 - m_4 + 2m_3 - 2m_2 + 3m_1 - 3m_0 &\geqslant -12,\\
M_6 - M_5 + M_4 - M_3 + M_2 - M_1 + M_0 + m_6 - m_5 + 2m_4 - 2m_3 + 3m_2 & \\
- 3m_1 + 4m_0 &\geqslant 20,
\end{aligned}
$$

Table 1
Spherical coordinates of the critical points found for three dipoles with the $D_{\infty h}$ connection (z is the $D_{\infty h}$ axis). The energy value is to be divided by R^3, R being the distance between two neighbouring dipoles. C_n and c_n point out non-linear and linear critical points with index n in the whole configuration space. In parenthesis, the number of equivalent configurations.

θ_1	ϕ_1	θ_2	ϕ_2	θ_3	ϕ_3	Index	Energy
0	0	0	0	0	0	c_0 (2)	−4.25
$\pi/2$	0	$-\pi/2$	0	$\pi/2$	0	C_1 (1)	−1.875
$\pi/2$	0	$\pi/2$	0	$-\pi/2$	0	C_2 (2)	−0.125
0	0	0	0	π	0	c_4 (4)	0.25
$\pi/2$	0	$\pi/2$	0	$\pi/2$	0	C_4 (1)	2.125
0	0	π	0	0	0	c_6 (2)	3.75

and the following equality holds:

$$m_6 - m_5 + m_4 - m_3 + m_2 - m_1 + m_0 = 8.$$

All these conditions are achieved by the set of critical points found numerically for $V(\theta_1, \phi_1, \theta_2, \phi_2, \theta_3, \phi_3)$ and given in table 1. More precisely, $M_0 = 0,\ M_1 = 1,\ M_2 = 2,\ M_3 = 0,\ M_4 = 1,\ M_5 = M_6 = 0,\ m_0 = 2,\ m_1 = 0,\ m_2 = 0,\ m_3 = 0,\ m_4 = 4,\ m_5 = 0$ and $m_6 = 2$.

All the critical points found on the hypersurface have their dipole vectors either all parallel or all perpendicular to the $D_{\infty h}$ axis. In the water trimer studied by Mó et al. [9] at different levels of calculation, some of these critical points are effectively obtained but among many other ones, showing that a multipole expansion of the potential beyond the dipole–dipole interaction is necessary in that case.

D_{3h}: the set of critical points is reported in table 2 and pictured in figure 1. Collecting, it is found that $M_0 = 2,\ M_1 = 12,\ M_2 = 18,\ M_3 = 6,\ M_4 = 6,\ M_5 = 2$ and $M_6 = 2$, in agreement with the Morse inequalities (equation (1) with $N = 3$):

$$\begin{aligned} M_0 &\geqslant 1, \\ M_1 - M_0 &\geqslant -1, \\ M_2 - M_1 + M_0 &\geqslant 4, \\ M_3 - M_2 + M_1 - M_0 &\geqslant -4, \\ M_4 - M_3 + M_2 - M_1 + M_0 &\geqslant 7, \\ M_5 - M_4 + M_3 - M_2 + M_1 - M_0 &\geqslant -7, \\ M_6 - M_5 + M_4 - M_3 + M_2 - M_1 + M_0 &= 8. \end{aligned}$$

Two non-trivial critical points with low symmetry and with a symmetry number equal to 12 do exist on the potential surface. One of them is a transition state, and thus of immediate chemical interest. The stable configuration C_0 ressembles the one reported by Mó et al. [9] (trimer 11) and by van Duijneveldt et al. [2] for the water

Table 2
C_n and C'_n critical points found for three dipoles at the vertices (0,0,0), $(\sqrt{3}R/2, -R/2, 0)$ and $(\sqrt{3}R/2, R/2, 0)$ of a R-side triangle, in the six (θ_i, ϕ_i) and three $(\theta_i = \pi/2, \phi_i)$ dimensional spaces, respectively. The energy value is to be divided by R^3. Angles are in radians. In parenthesis, the number of equivalent configurations.

θ_1	ϕ_1	θ_2	ϕ_2	θ_3	ϕ_3	Index	Energy
$\pi/2$	$\pi/2$	$\pi/2$	$-5\pi/6$	$\pi/2$	$-\pi/6$	C_0 C'_0 (2)	-3.75
$\pi/2$	π	$\pi/2$	2.588	$\pi/2$	-2.588	C_2 C'_1 (6)	-2.22
$\pi/2$	$\pi/2$	$\pi/2$	0.109	$\pi/2$	$\pi - 0.109$	C_4 C'_2 (6)	$+1.63$
$\pi/2$	0	$\pi/2$	$2\pi/3$	$\pi/2$	$-2\pi/3$	C_6 C'_3 (2)	$+5.25$
0	0	0.864	2.536	$\pi - 0.864$	-2.536	C_1 (12)	-2.34
0.16	$-\pi/2$	1.911	-1.337	1.911	$-\pi + 1.337$	C_2 (12)	-2.29
0	0	π	0	π	0	C_3 (6)	-1.00
0	0	0	0	0	0	C_5 (2)	$+3.00$

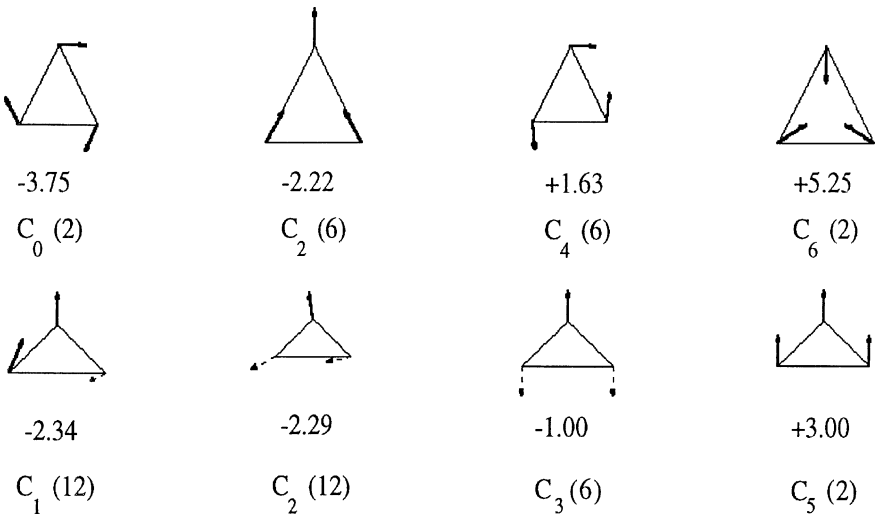

Figure 1. Critical points C_n with index n found for three interacting dipoles at the top of an equilateral R-side triangle. The energy value is to be divided by R^3. In parenthesis, the number of equivalent configurations.

trimer. The point stresses that, despite the lack of dipole–quadrupole interactions, our asymptotic study can predict at least some of the critical points for actual potential functions. It actually does generically, as long as no bifurcation occurs from higher order contributions.

In table 2, are given the indices of the C'_n "planar" critical points (each value for θ_i is $\pi/2$ and the space is spanned by ϕ_1, ϕ_2, ϕ_3). Betti numbers for this cross-section come from $(1+t)^3$, the three-dimensional torus, and lead to the following

right-members in the Morse inequalities: (1,2,1,0). The actual numbers of "planar" critical points ($M'_0 = 2,\ M'_1 = 6,\ M'_2 = 6$ and $M'_3 = 2$) match them:

$$\begin{aligned} M'_0 &\geqslant 1, \\ M'_1 - M'_0 &\geqslant 2, \\ M'_2 - M'_1 + M'_0 &\geqslant 1, \\ M'_3 - M'_2 + M'_1 - M'_0 &= 0. \end{aligned}$$

3.3. *Interaction between four dipoles*

Four types of clusters have been studied. Betti numbers are found by developping either $(1+t^2)^4/(1-t^2)$ or $(1+t^2)^4$ according to the case where the connections of the dipole vectors are aligned or not (see equations (1) and (2)). This leads to the following right-members in the inequalities: $(1,-1,6,-6,17,-17,32,-32,48)$ and $(1,-1,5,-5,11,-11,15,-15,16)$, respectively.

$D_{\infty h}$: as for the $D_{\infty h}$ connections between three dipoles, the $D_{\infty h}$ connection for four dipoles leads to critical points for which all the vectors are either parallel or perpendicular to the z-axis (connection axis). The corresponding c_n and C_n critical points with their symmetry number are as follows (parenthesized values are energies for each R-distance between neighbouring dipoles equal to one): $C_1 = 1$ (-2.79), $C_2 = 3$ (-1.21), $C_4 = 3$ (0.96), $C_6 = 1$ (3.29), $c_0 = 2$ (-6.57), $c_4 = 6$ (-1.93), $c_6 = 6$ (1.93) and $c_8 = 2$ (5.57). Thus, $M_0 = 0,\ M_1 = 1,\ M_2 = 3,\ M_3 = 0,\ M_4 = 3,\ M_5 = 0,\ M_6 = 1,\ M_7 = M_8 = 0,\ m_0 = 2,\ m_1 = m_2 = m_3 = 0,\ m_4 = 6,\ m_5 = 0,\ m_6 = 6,\ m_7 = 0$ and $m_8 = 2$; equation (2) is met for $N = 4$. It may be pointed out that each of the left-members in the inequalities, except the first one, equals the right-members, a strong evidence that the potential function is one of the simplest ones.

D_{3h} (table 3 and figure 2): the critical points have all their dipole vectors either in the D_{3h} plane (xy) or perpendicular to that plane. From the twelve critical configurations found, eight of them are "planar" ($\theta_i = \pi/2$). The "planar" cross-section is 4-dimension, spanned by $\phi_1, \ldots, \phi_4$. We name C'_n the index of the 8 critical points restricted within this subspace. The Betti numbers arise from $N = 4$ in equation (3), delivering Morse inequalities with right members (1,3,3,1,0). In both spaces (4- and 8-dimensional, 8 and 12 critical points, respectively), equations (3) and (1) are met with $N = 4$.

D_{4h}: in table 4 are reported all the critical points found on the hypersurface. Equations (1) and (3) for $N = 4$ are once more verified. However, unlike D_{3h} case, two configurations with low symmetry and for which dipole vectors are neither parallel nor perpendicular to the D_{4h} plane have been found (C_3(16) and C_5(16)).

T_d: we report in table 5, the (θ_i, ϕ_i) dipole directions for each critical points, the coordinates of their origin being (0,0,0), $(\sqrt{3}R/2, -R/2, 0)$, $(\sqrt{3}R/2, R/2, 0)$ and

Table 3
C_n and C'_n critical points found for four dipoles at the vertices (0,0,0), $(\sqrt{3}R/2, -R/2, 0)$, $(\sqrt{3}R/2, R/2, 0)$, and at the center $(\sqrt{3}R/3, 0, 0)$ of a R-side triangle, in the eight (θ_i, ϕ_i) and four $(\theta_i = \pi/2, \phi_i)$ dimensional spaces, respectively. The energy value is to be divided by R^3. Angles are in radians. In parenthesis, the number of equivalent configurations.

θ_1	ϕ_1	θ_2	ϕ_2	θ_3	ϕ_3	θ_4	ϕ_4	Index	Energy
$\pi/2$	0	$\pi/2$	-1.578	$\pi/2$	1.578	$\pi/2$	0	C_0 C'_0 (6)	-24.491
$\pi/2$	$\pi/2$	$\pi/2$	-0.946	$\pi/2$	$-\pi + 0.946$	$\pi/2$	$-\pi/2$	C_1 C'_1 (6)	-24.173
$\pi/2$	$\pi/2$	$\pi/2$	2.433	$\pi/2$	$\pi - 2.433$	$\pi/2$	$\pi/2$	C_2 C'_1 (6)	-16.579
$\pi/2$	0	$\pi/2$	1.063	$\pi/2$	-1.063	$\pi/2$	π	C_4 C'_2 (6)	0.151
$\pi/2$	0	$\pi/2$	1.565	$\pi/2$	-1.565	$\pi/2$	0	C_5 C'_2 (6)	7.706
$\pi/2$	$\pi/2$	$\pi/2$	2.308	$\pi/2$	$\pi - 2.308$	$\pi/2$	$-\pi/2$	C_6 C'_3 (6)	10.572
$\pi/2$	$\pi/2$	$\pi/2$	-0.614	$\pi/2$	$-\pi + 0.614$	$\pi/2$	$\pi/2$	C_7 C'_3 (6)	24.218
$\pi/2$	0	$\pi/2$	-1.951	$\pi/2$	1.951	$\pi/2$	π	C_8 C'_4 (6)	24.270
0	0	0	0	0	0	π	0	C_2 (2)	$3 - 9\sqrt{3}$
0	0	π	0	π	0	0	0	C_3 (6)	$-1 - 3\sqrt{3}$
0	0	π	0	π	0	π	0	C_4 (6)	$-1 + 3\sqrt{3}$
0	0	0	0	0	0	0	0	C_6 (2)	$3 + 9\sqrt{3}$

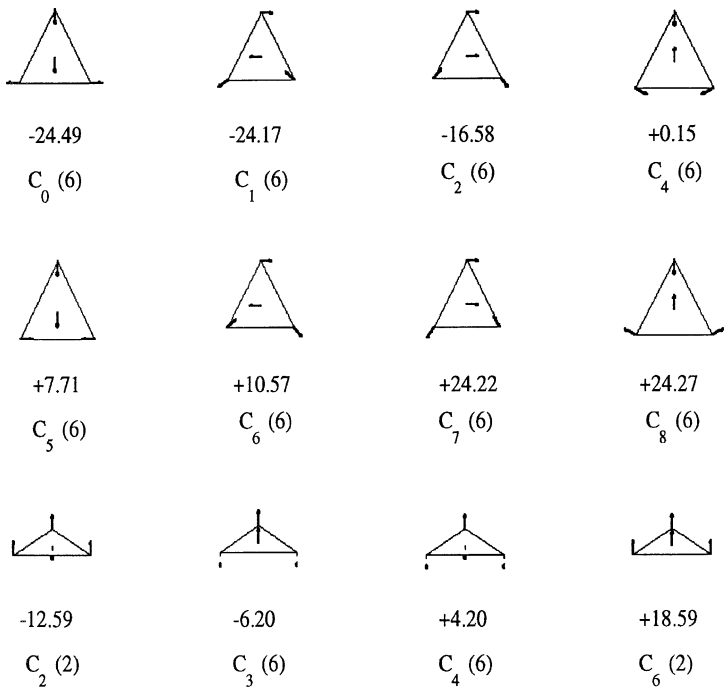

Figure 2. Critical points C_n found for four interacting dipoles at the top and the middle of an equilateral R-side triangle. The energy value is to be divided by R^3. In parenthesis, the number of equivalent configurations.

Table 4
C_n and C'_n critical points found for four dipoles at the vertices (0,0,0), (R,0,0), (R,$-R$,0) and (0,$-R$,0) of a R-side square, in the eight (θ_i, ϕ_i) and four $(\theta_i = \pi/2, \phi_i)$ dimensional spaces, respectively. The energy value is to be divided by R^3. Angles are in radians. In parenthesis, the number of equivalent configurations.

θ_1	ϕ_1	θ_2	ϕ_2	θ_3	ϕ_3	θ_4	ϕ_4	Index	Energy
$\pi/2$	$\pi/4$	$\pi/2$	$-\pi/4$	$\pi/2$	$-3\pi/4$	$\pi/2$	$-5\pi/4$	C_0 C'_0 (2)	$-6+1/\sqrt{2}$
$\pi/2$	$3\pi/4$	$\pi/2$	$-3\pi/4$	$\pi/2$	$-\pi/4$	$\pi/2$	$\pi/4$	C_1 C'_1 (2)	$-6+\sqrt{2}$
$\pi/2$	$-\pi/2+0.244$	$\pi/2$	$-\pi/2-0.244$	$\pi/2$	$-\pi/2+0.244$	$\pi/2$	$-\pi/2-0.244$	C_2 C'_1 (4)	-2.617
$\pi/2$	$-3\pi/4$	$\pi/2$	$-3\pi/4$	$\pi/2$	$-3\pi/4$	$\pi/2$	$-3\pi/4$	C_2 C'_1 (4)	$-2-1/2\sqrt{2}$
$\pi/2$	$\pi/2+0.010$	$\pi/2$	-1.738	$\pi/2$	$-\pi/2+0.010$	$\pi/2$	-1.383	C_4 C'_2 (16)	0.011
$\pi/2$	$\pi/4$	$\pi/2$	$-3\pi/4$	$\pi/2$	$\pi/4$	$\pi/2$	$-3\pi/4$	C_6 C'_3 (4)	$2-1/2\sqrt{2}$
$\pi/2$	$-\pi/2-1.327$	$\pi/2$	$-\pi/2+1.327$	$\pi/2$	$-\pi/2-1.327$	$\pi/2$	$-\pi/2+1.327$	C_6 C'_3 (4)	1.910
$\pi/2$	$\pi/4$	$\pi/2$	$3\pi/4$	$\pi/2$	$-3\pi/4$	$\pi/2$	$-\pi/4$	C_7 C'_3 (2)	$6-1\sqrt{2}$
$\pi/2$	$3\pi/4$	$\pi/2$	$\pi/4$	$\pi/2$	$-\pi/4$	$\pi/2$	$-3\pi/4$	C_8 C'_4 (2)	$6+\sqrt{2}$
0	0	π	0	0	0	π	0	C_2 (2)	$-4+1/\sqrt{2}$
3.392	1.480	1.073	-1.836	1.073	$-\pi+1.836$	-3.392	-1.480	C_3 (16)	-1.413
0	0	π	0	π	0	0	0	C_4 (4)	$-1/\sqrt{2}$
0	0	π	0	π	0	π	0	C_4 (8)	0
0.352	-3.087	$\pi-0.352$	$-\pi+3.087$	$\pi-1.333$	$-\pi+0.255$	1.333	-0.255	C_5 (16)	0.742
0	0	0	0	0	0	0	0	C_6 (2)	$4+1/\sqrt{2}$

Table 5
Critical points found for four dipoles with the T_d connection (see text for vertices coordinates). The energy value is to be divided by R^3, R being the distance between two neighbouring dipoles. Angles are in radians. α is a peculiar value (0.61548) corresponding to the half-angle made by two mediators of T_d faces from the middle of an edge. In parenthesis, the number of equivalent configurations.

θ_1	ϕ_1	θ_2	ϕ_2	θ_3	ϕ_3	θ_4	ϕ_4	Index	Energy
$\pi+\alpha$	$2\pi/3$	$\pi/2$	$\pi/6$	$-\alpha$	$-\pi/3$	$-\pi/2$	$\pi/6$	C_0 (6)	-5.000
0.5669	0.6588	2.6503	1.7267	-1.2138	-1.6511	1.4493	-0.8755	C_1 (24)	-4.625
2.5815	0	α	0	α	0	-1.3506	0	C_2 (12)	-4.449
1.3467	$0.7678-2\pi/3$	1.3467	0.7678	1.3467	$0.7678+2\pi/3$	0	0	C_2 (16)	-4.583
1.4595	0	2.0169	-0.8279	2.0169	0.8279	2.9130	0	C_3 (6)	-3.772
0.5564	0	0.5564	$2\pi/3$	0.5564	$4\pi/3$	0	0	C_3 (8)	-1.161
0.5085	0	1.8804	0.9010	1.8804	-0.9010	0.0680	0	C_4 (24)	-0.700
-0.3398	0	2.0617	0.7137	2.0617	-0.7137	$-\pi/2$	0	C_5 (6)	1.000
-0.4753	-0.8136	1.7447	0.5857	2.3691	-0.8948	$-\pi/2$	0.3391	C_5 (12)	1.000
-0.3787	-0.4767	1.9029	0.6458	2.2180	-0.7942	$-\pi/2$	0.1704	C_6 (12)	1.000
$3\pi/2$	$3\pi/2$	2.1773	0.1945	$\pi-2.1773$	$\pi-0.1945$	$3\pi/2$	$3\pi/2$	C_6 (24)	4.322
6.1719	0	1.1771	4.0845	-1.1771	$\pi-4.0845$	4.4838	0	C_7 (24)	4.772
2α	0	2α	$2\pi/3$	2α	$4\pi/3$	π	0	C_8 (2)	10.000

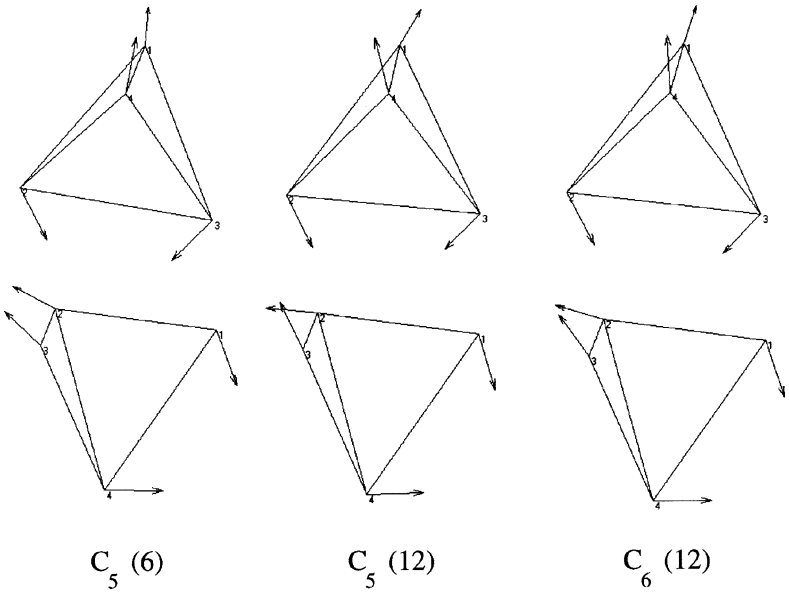

Figure 3. Two projections of the three different critical points with the same energy (T_d connections).

($\sqrt{3}R/3, 0, \sqrt{2/3}R$). Three close but unequivalent configurations[1] have the same energy ($V = 1.000 \times R^{-3}$) and are almost degenerated (one or two Hessian eigenvalues are close to zero) showing that the potential is very flat in this region (see figure 3). The indices found for these critical points agree with the Morse inequalities, but the absence of other critical points with lower symmetry cannot be ascertained numerically in the same region.

Once again, some of our configurations can be found among the numerous stationary points obtained by Wales and Walsh for the water tetramer [16]. Particularly, our C_0 minimum for the D_{4h} connections (table 4) is very similar to the planar C_{4h} critical point given in their work even if it is not the most stable configuration owing to the use of a rigid monomer intermolecular potential with an anisotropic site potential (ASP) form.

4. Conclusions

In this generic study of van der Waals systems, we stressed the advantages to make use of topology theorems available in fully explicit form. The imbricated sets of Morse inequalities are the key points to validate any numerical approach to the critical points (except accidental pleats) on the potential hypersurface.

[1] An efficient test that two configurations with the same energy are not equivalent is the projections of the dipole vectors on each couple of connections: configurations are dissimilar if some absolute values differ after possible permutations.

Betti numbers are reported for the potential functions describing any set of N monomers, provided the orientation of each monomer is specified by two angles only: systems exactely linear (diatomics, acetylene [1], ...) or assimilated (e.g., CH_3CN up to the quadrupole level of description). In the case of N identical monomers with a permanent dipole, the asymptotic study of N interacting dipoles should be realistic enough to locate the whole sets of critical points on actual van der Waals potential surfaces, generally represented in the literature by only one or several minima and saddle points. Surprisingly, the first term of a multipole expansion of the interaction energy between three or four molecules immediately lead to a complex potential hypersurface: more than ten unequivalent critical points are found for four-body systems in each non-linear geometry (D_{3h}, D_{4h} and T_d). More, the surfaces of these van der Waals supersystems are very flat: for example in the T_d geometry, the energy range between the critical points is 15×10^{-3} a.u. $\simeq 3300$ cm^{-1} for a R-side value equal to 10 a.u. and for which the sole dipole–dipole interaction predominates (exchange potential becoming insignificant beyond this R-value). For smaller distances, we can expect that the subspaces of the N vector connections ($D_{\infty h}, D_{3h}, D_{4h}, T_d, \ldots$) remain separated by high energy barriers so that the local studies still hold. That means also there is no interpenetration of atoms between molecular fragments.

In the future, it would be interesting to analyse the topological bifurcations encountered by the potential function when a non-additive many-body intermolecular potential is used like that one of McDowell [7] for the H_2 trimer. More, to study the hypersurface of H_2O clusters as in [9,16], dipole–quadrupole and quadrupole–quadrupole interactions should be added to account for the molecular planarity and its orientations. In that case, an open question of topolgy consists in the elucidation of the Betti numbers for the configuration space.

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