Structure and Dynamics of Molecular Systems

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PREFACE

This volume is the first of a set of two which contain the invited lectures given at the international seminar of the same title held at the Centre de Mécanique Ondulatoire Appliquée du Centre National de la Recherche Scientifique in Paris (France) from October 1983 to May 1985. They are intended to provide a survey of topics of current interest relative to the structure and the dynamics of molecular systems. The papers have been selected on the basis of their relevance to the following four topics: i) molecular conformations and transformations; ii) molecular relaxation and motion; iii) charge, spin and momentum distributions in molecular solids; iv) collective phenomena in condensed matter. The first volume deals mostly with the first two topics, the second volume mostly with the last two. Each volume consists of about fifteen self-contained, reference contributions covering recent achievements in active branches of molecular physics and physical chemistry.

The first four papers of the present volume deal with theoretical aspects of structure and reactivity problems, with particular attention being paid to topology considerations, which have joined symmetry considerations as an important tool in approaching chemistry problems. The treatment of nuclear probability density distributions is performed on a model basis for a simple system, even though it has come to the attention of theoreticians through experimental results for complex systems. The following six papers are relevant to particular phenomena occurring in disordered solids as well as in mixed crystals: spatial or spectral localization of electronic or magnetic excitation, fractal structures, random walks, cross relaxation, triplet annihilation as well as chemical reactions. The last five papers deal with the structural and dynamical information one can derive from magnetic resonance and relaxation techniques for such systems as model membranes, liquid crystals, gel phases, micelles and interfaces. Many of these papers contain an abundant bibliography which should help the interested reader go deeper into the subject.

The editors wish to express their gratitude to the Direction de la Chimie of the C.N.R.S. for lending financial support to the International seminar.

THE EDITORS

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FROM THEORETICAL CHEMISTRY TO MOLECULAR SHAPE AND REACTIVE TRANSFORMATION

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ABSTRACT. In the present work we will try to show how theoretical chemistry can be a tool for analysing some chemical events such as the recognition and the classification of the molecular forms, or such as the reactive transformation of the molecules.

Starting with the Born-Oppenheimer approximation, we can separate the electronic motion from the nuclear one. This approximation gives rise to a useful concept: the potential energy (hyper)surface, on which the nuclei are moving. Then, with the help of Thom's concepts, we can try to analyse the potential surface and partition it into molecular regions. After having considered the eigenvalues of the electronic equation, we can go further and, with the help of the theory of graphs, define an electronic picture for any molecular structures, including those which appear along the reaction pathway: we thus obtain the so-called electronic reaction mechanism.

1. FROM THE POTENTIAL ENERGY SURFACE (PES) TO THE MOLECULAR SHAPE

1.1. PES and Born Oppenheimer approximation

The time independent Schrödinger equation for a molecular system which contains N nuclei and n electrons is :

$$\mathcal{H}(r,R)\, Y(r,R) = W Y(r,R) \qquad (1)$$

where the total hamiltonian $\mathcal{H}$ stands for :

$$\mathcal{H} = -\frac{1}{2}\sum_{a}^{N}\frac{\Delta_a}{m_a} - \frac{1}{2}\sum_{i}^{n}\Delta_i - \sum_{a,i}^{N,n}\frac{Z_a}{|r_i-R_a|} + \frac{1}{2}\sum_{i\neq j}^{n,n}\frac{1}{|r_i-r_j|}$$
$$+ \frac{1}{2}\sum_{a\neq b}^{N,N}\frac{Z_a Z_b}{|R_a-R_b|}$$

Then, it contains kinetic (T) and potential (V) operators :

R. Daudel et al. (eds.), Structure and Dynamics of Molecular Systems, 1–22.

$$\mathcal{H} = \underbrace{T_N(R)}_{\mathcal{H}^{(1)}} + \underbrace{T_E(r) + V(r,R)}_{\mathcal{H}^{(0)}}$$

As the kinetic operator relative to the nuclei (T_N) is proportional to the inverse of the nucleus mass (m_a, $\forall$ $a = 1, N$) which is larger than the electron mass (m_e), we can consider T_N as a perturbation with respect to the remaining part of $\mathcal{H}$. Using the Rayleigh-Schrödinger perturbation theory, we find a zeroth order wave-equation which does not contain any more the T_N term$^{(1)}$:

$$\{T_E(r) + V(r|R)\} \Psi(r|R) = E(|R) \Psi(r|R) \qquad (2)$$

This is the so-called electronic equation; it describes the electron motion in the fixed nucleus field. Their eigenvectors ($\Psi(r|R)$) as well as their eigenvalues ($E(|R)$) are defined parametrically to the nuclear coordinates (R). At the first order of the perturbational treatment, we find the total wavefunction ($Y(r,R)$). Let us expand Y in the basis of the eigenvectors of (2). Then, if the following approximations may be assumed (the Born-Oppenheimer approximations) :

$$Y(r,R) = \sum_\mu \chi_\mu(R) \Psi_\mu(r,R) \simeq \chi_\mu(R) \Psi_\mu(r|R) \qquad (3a)$$

$$< \Psi_\mu | \nabla_R | \Psi_\nu >_r \simeq 0 \qquad (3b)$$

the first order wave-equation becomes :

$$\{T_N(R) + E_\mu(R)\} \chi_\mu(R) = W_\mu \chi_\mu(R) \qquad (4)$$

This is the so-called nuclear equation, which describes the motion of the nuclei in the potential energy field E(R). We conclude that, as long as we can put the relations (3) into practice, we can describe separately the motion of the electrons (eq.(2)) from this of the nuclei (eq. (4)); moreover, the eigenvalues of (2) must be considered as a potential energy hypersurface for the nuclear motion; this last concept comes from the B.O. approximation.

The potential energy surface is a function of the 3N cartesian coordinates for the N nuclei :

$$E = E(\vec{R}) = E(\vec{R}_1,\ldots,\vec{R}_N) = E(X_1 Y_1 Z_1,\ldots,X_N Y_N Z_N) \qquad (5)$$

Nevertheless, it remains invariant under global rotation and translation for the entire system. We further define a new coordinate frame (s), which only contains 3N-6 independent variables :

$$E = E(\vec{s}) = E(s_1,\ldots,s_k) \qquad \text{with} \quad k = 3N-6 \qquad (6)$$

s is the so-called internal coordinate system. We can also define an other frame, the internal displacement system S, related to the previous one by :

$$\vec{S} = \vec{s} - \vec{s}_o = \{ S_1, \ldots, S_k \} \tag{7}$$

This last frame is of any use to write a local analytical form for the potential surface. So, let us expand the potential in a Taylor series:

$$E(\vec{S}) = E_o + \vec{g}'_o \vec{S} + \frac{1}{2} \vec{S}' \tilde{H}_o \vec{S} + \ldots \tag{8}$$

where $E_o = E(S = o) = E(s_o)$

$\vec{g}_o = (\vec{\nabla}_S E(S))_{S=o}$: the potential energy gradient

$\tilde{H}_o = (\vec{\nabla}'_S \vec{\nabla}_S E(S))_{S=o}$: the force constant matrix

In solving the equation (2) for s_o, we obtain E_o :

$$E_o = \frac{<\Psi(r|R_o) \mid \mathcal{H}(r|R_o)^{(o)} \mid \Psi(r|R_o)>_r}{<\Psi(r|R_o) \mid \Psi(r|R_o)>_r} \tag{9}$$

By differentiating this last relation with respect to s (at $s = s_o$), we find analytical estimates of g_o and H_o (1-6). However, this is not always feasible, specially beyond the SCF level; in such cases g_o and H_o are only available from numerical approach(7-9).

1.2. PES and stationary points

The relation (8) is of great interest because it enables one to locate stationary points and to know the local surface curvature. A stationary point is a point of the potential energy surface where the gradient vector $g_\blacksquare$ vanishes :

$$\text{If} \quad \vec{g}_\blacksquare = \vec{o}$$

$$\text{then} \quad \vec{S}_\blacksquare = - \tilde{H}_o^{-1} \vec{g}_o \tag{10a}$$

$$\text{and} \quad \vec{s}_\blacksquare = \vec{s}_o - \tilde{H}_o^{-1} \vec{g}_o \tag{10b}$$

If we translate the origin of the Taylor expansion at the stationary point and rotate the internal coordinate frame in such a way as to diagonalise the force constant matrix, the potential function takes the simple form :

$$\text{if} \quad \tilde{U}' \tilde{H}_o \tilde{U} = \tilde{h} \text{ (diagonal)} \qquad \text{with} \quad \tilde{U}' \tilde{U} = \tilde{1}$$

$$\text{and} \quad \vec{V} = \tilde{U}' (\vec{S} - \vec{S}_\blacksquare)$$

$$E(\vec{V}) = E_\blacksquare + \frac{1}{2} \vec{V}' \tilde{h} \vec{V} \tag{11a}$$

or $$\Delta\vec{E}(V)_{\blacksquare} = E(\vec{V}) - E_{\blacksquare} = \frac{1}{2}\sum_{i=1}^{k} V_i^2\, h_{ii} \qquad (11b)$$

That means the energy variation, which occurs when we are leaving the stationary point, depends on the diagonal h_{ii} terms. So the current stationary point corresponds to an absolute or an asymptotic maximum ($\Delta E(\vec{V}) \geqslant 0$, $\nabla\vec{V}$) if h is a positive or semi-positive defined matrix(10) :

$$g_i = 0 \quad \text{and} \quad h_{ii} \geqslant 0 \qquad \nabla i = 1, k \qquad (12)$$

The corresponding nuclear structure is a stable equilibrium structure (see Figure 1).

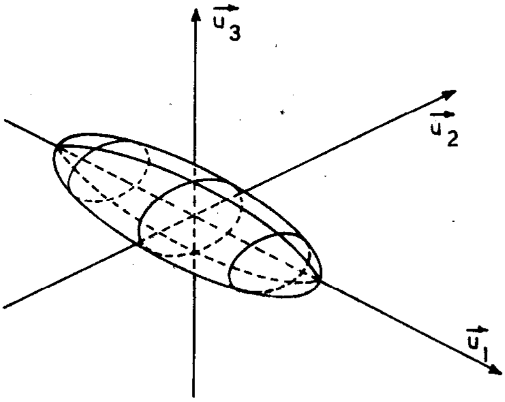

Figure 1. Potential isoenergy surface around a stationary point corresponding to an equilibrium structure in a 3-dimension internal coordinate space.

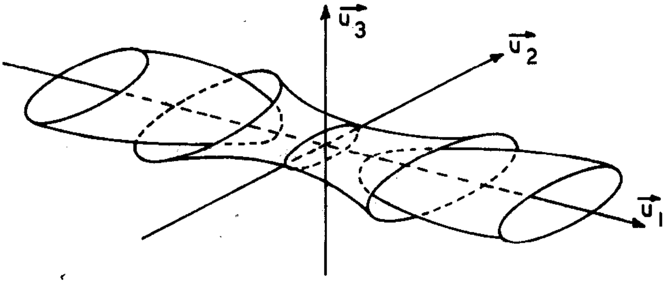

Figure 2. Potential isoenergy surfaces around a stationary point of first order minimax type in a 3-dimension internal coordinate space.

Another critical point is of particular chemical interest: the first order minimax (see Figure 2), which can be defined in the following way :

$$g_I = o,\ h_{II} < o,\ g_i = o \text{ and } h_{ii} > o \qquad \forall i = 2, k \tag{13}$$

Murrell and Laidler(11) showed that, as long as a potential barrier separates the reactants from the products, a first order minimax (also called saddle point) is the highest energy point lying on the lowest energy path between both reactants and products. As shown on Figure 3, if this highest energy point is a minimax of order greater then one, it exists a path "A" of lower energy than the path "B", path "A" which does not cross such a minimax.

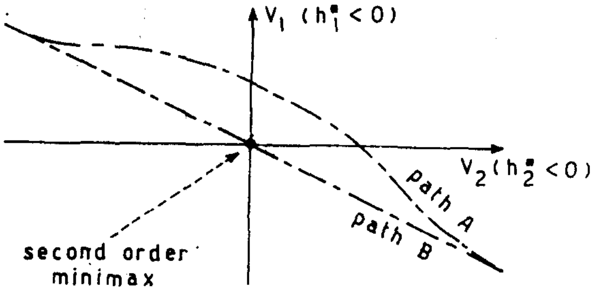

Figure 3. The first order minimax is the highest energy point on the lowest energy path which connects reactants and products as long as a potential barrier separates both.

1.3. PES and reaction pathway

Some define the reaction path as the lowest energy path connecting reactants and products on the potential surface(12) or alternately as the path of highest slope starting from the highest energy point of the previous lowest energy path(13). Those definitions are incomplete(14-17). We can prove this statement as follow: let us suppose a potential energy surface (E) described in two coordinate frames (S and V) related to each other by the local relation :

$$\vec{S} = \tilde{U}\vec{V} \tag{14}$$

On the one hand, the first order derivatives of E in both frames are related using the chain rule by :

$$\vec{g}(V) = \tilde{U}'\vec{g}(S) \tag{15}$$

On the other hand, as $\vec{g}(S)$ is a vector, its direction on the E(V) surface will be given by :

$$\vec{d}(V) = \tilde{U}^{-1}\vec{g}(S) \tag{16}$$

From (15) and (16), we find that g(V) and d(V) are only identical if :

$$\vec{g}(S) = \vec{o} \qquad \text{for any } U \tag{17a}$$

$$\text{or} \quad \tilde{U}' = \tilde{U}^{-1} \quad \text{for any } g(S) \tag{17b}$$

Equation (17a) tells that the stationary points location does not depend on the coordinate frame in use, this is an intrinsic property. In other respects, (17b) shows the non-intrinsic character of the paths as long a U is not a unitary transformation matrix. The Figure 4 illustrates this point. The steepest descent paths which connect the reactants and the products on E(S) and E(V) surfaces are only confused at the stationary points.

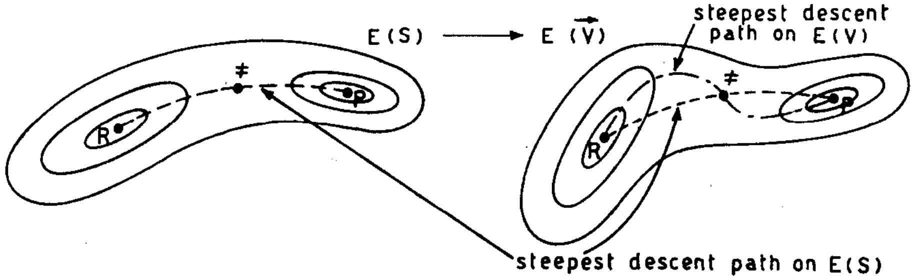

Figure 4. Steepest descent reaction pathway on a potential energy surface expressed in S or V coordinate frames.

Some years ago Fukui et al.(15) have introduced the concept of intrinsic reaction pathway. This concept has been expressed more recently in terms of internal coordinate frame(17). We know that the classical equations of Lagrange describe the motion independently with respect to the coordinate frame in use. So we have :

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{S}} + \frac{\partial E}{\partial S} = o \tag{18}$$

$$\text{with} \quad E = E_o + \vec{g}_o'\vec{S} + \frac{1}{2}\vec{S}'\tilde{H}_o\vec{S} \tag{19a}$$

$$\text{and} \quad T = \frac{1}{2}\dot{\vec{\xi}}'\tilde{M}\dot{\vec{\xi}} = \frac{1}{2}\dot{\vec{S}}'\tilde{G}^{-1}\dot{\vec{S}} \tag{19b}$$

if $\tilde{G} = \tilde{B}\tilde{M}^{-1}\tilde{B}'$ (the G matrix of Wilson(18))

and $\vec{S} = \tilde{B}\vec{\xi} = \tilde{B}(\vec{R} - \vec{R}_o)$

Then, the motion equations become :

$$\ddot{\vec{S}} + \tilde{G}\vec{g}_o + \tilde{G}\tilde{H}_o\vec{S} = \vec{o} \tag{20}$$

Those second order differential equations can be uncoupled by using a coordinate frame which diagonalizes the product GH; the relation (20) becomes now :

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$$\vec{\Gamma} = - \{\vec{\nabla}_Q(\vec{F}'(Q)\,\vec{F}(Q))^{1/2}\}_{Q=o} = - \tilde{\Lambda}\,\vec{g}/(\vec{g}'\,\vec{g})^{1/2} \qquad (23)$$

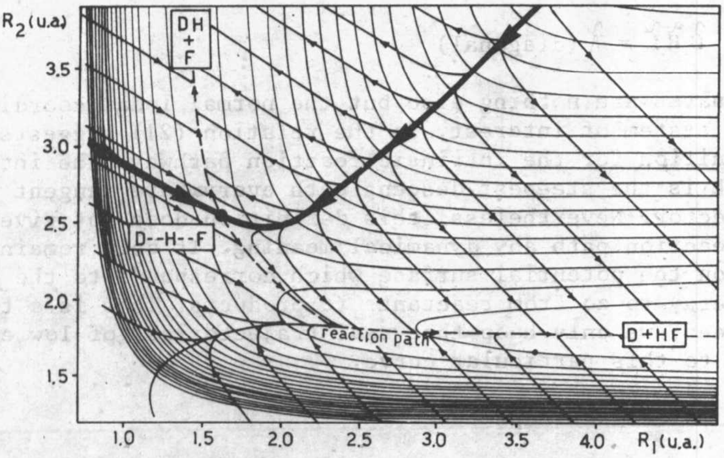


Figure 5. Space partition into basins through the force field.

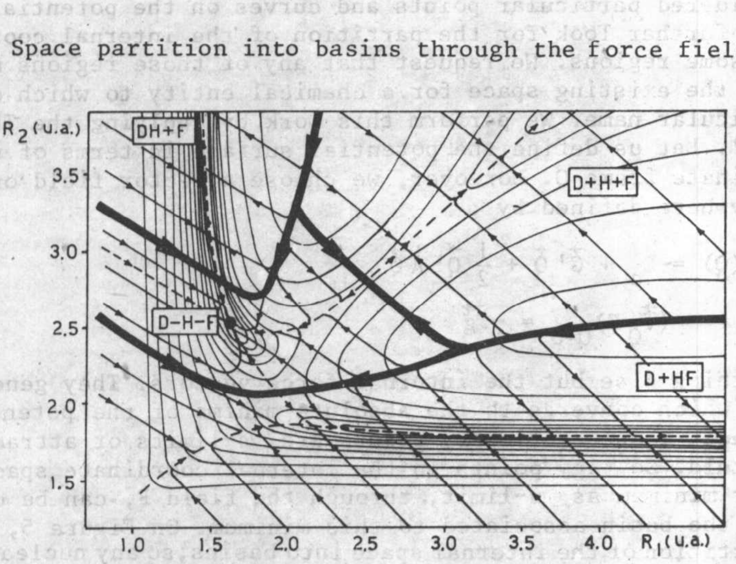
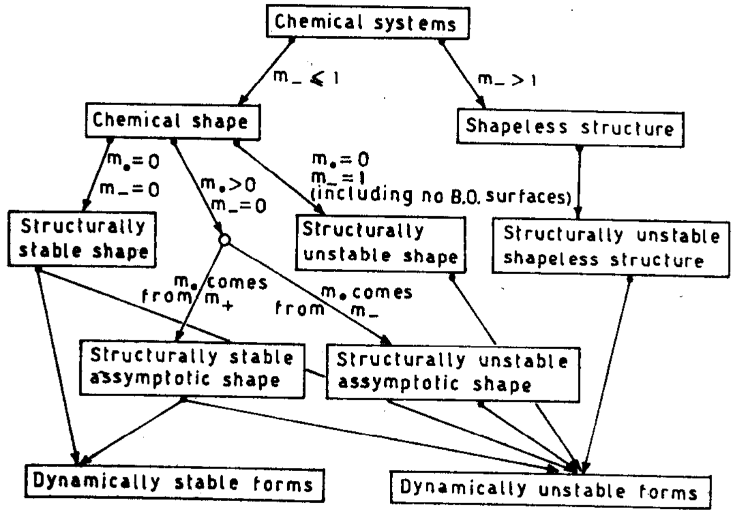


Figure 6. Space partition into basins through the gradient of the force norme.

Any stationary point on E becomes a minimum on |F| surface. The number of attractors increases from the first description. The basin number increases in the same way but their size are reduced. As shown on Figure 6, we find new basins which are associated to minimax (transition basin) or maximum (dissociation basin). We note also that minimax appear on the Force norm surface, in particular along the reaction paths and on the basins boarders; their correspond to inflexion points lying on the potential surface. So, we further consider the basins of the Figure 6 as the regions in the internal coordinate space surrounding a stationary point where the eigenvalues of the force constant matrix keep the same signs.

The internal coordinate space partition enables us to go from a continuous representation of the chemical systems to a discrete set of names and existence regions. Moreover, we dispose now of a mean to classify the chemical forms. If m_0 and m_- stand respectively for the number of zero and negative eigenvalues associated to a stationary point (having a basin in charge), then we can find the following classification:



The local potential energy surface curvature is responsible for the structural stability. Any structurally unstable chemical forms can never be expected as having a long live time. On another hand the structurally stable forms are only persistent if their are dynamically stable. Indeed, the width of the nuclear motion is closely related to the translational-, rotational- and vibrational state of the system of interest.

1.5. PES : a useful tool

The potential energy surface, which exists in the Born-Oppenheimer approximation frame, is an help in the molecular analysis. As previously shown, it enables to recognize the molecular forms and to classify them. The capabilities of this tool can be summarized as follow :

-1- Recognition of the chemical forms: any stationary point of the PES being their first representation moment;

-2- Classification of the chemical forms in terms of their structural stabilities: the local curvature of the PES around the stationary points;

-3- Recognition of the connexion paths from a chemical form to an other one: the intrinsic reaction pathway on the PES which is the first representation moment of the chemical transformation;
-4- Recognition of the existence domain for the chemical forms: the basin associated to any stationary point in the gradient field of the force norm;
-5- Classification of the chemical forms in terms of their dynamical stabilities: the accessible region on the PES at a given temperature; this is the second moment of the chemical representation.

So, the PES leads to an explicit description in terms of nuclear structure. Moreover, the PES contains the energy description of the molecular forms :

-1- The first moment of the energetical description of a chemical form is given by the total energy of the associated stationary point;
-2- The first moment of the description of the chemical transformation from the energetical view point is given by the energy differences between stationary points lying along the reaction pathway;
-3- The second moment of the previous representations will be obtained by correcting the related energy values for the temperature dependence.

To fulfil the previous molecular representation, we have still to complete it by the electronic structure description. In fact, this last is implicitely contained in the potential energy surface. We have only considered in this section the eigenvalues of the equation (2), while the electronic description comes from the eigenvectors of the same equation (2).

2. FROM THE MOLECULAR SHAPE TO THE ELECTRONIC STRUCTURE AND CHEMICAL REACTIVITY

2.1. The electronic structure from the wavefunction

The problem is now how to obtain a simple picture of the electronic structure for a given chemical form and how to describe its evolution along a reaction pathway. As molecule can be regarded as atoms at finite distances from each other, bridged by an electronic cloud, a picture in terms of vertices and edges seems suitable in order to represent the molecular cohesion; that is nothing else that a graph. Untill now, the quantum chemistry has estabished two different approaches for obtaining such electronic graphs.

The Bader's approach(21-22) is first of all a topological analysis of the electron density. As shown on Figure 7, the map of the gradient density path enables to partition the R^3 space into different atomic volumes. Such volumes can be classify in two groups (depending on the fact that the atom have or no lone pairs) and three subgroups (depending on the number of surrounding atoms), as shown on Figure 8.

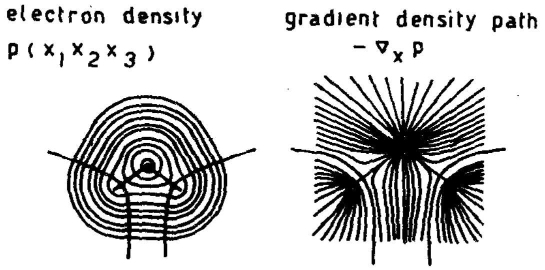


Figure 7. Space partition into atomic regions using Bader's topological approach.

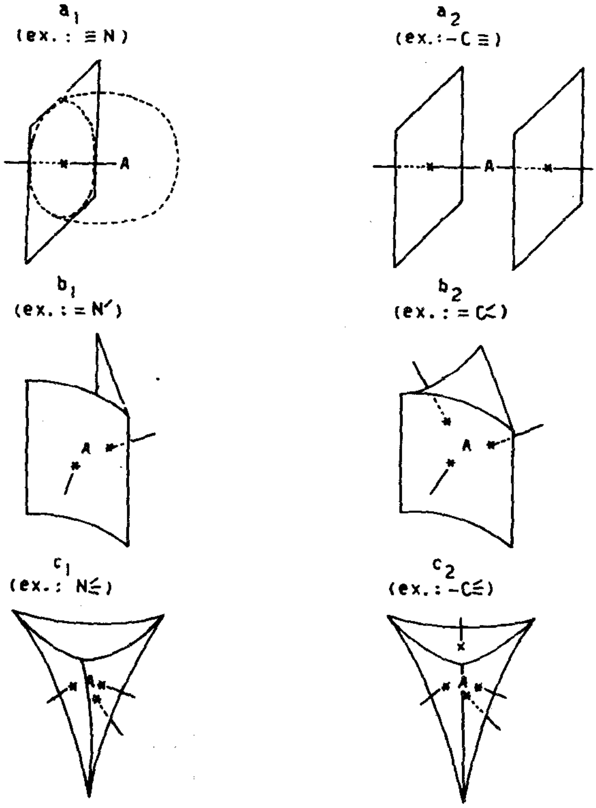


Figure 8. Different types of atomic regions using the Bader's topological approach.