Theor Chim Acta (1992) 83: 433–440

Theoretica Chimica Acta

© Springer-Verlag 1992

A global strategy for determining reaction paths

I. General theory of a procedure finding Fukui's intrinsic reaction coordinate*

László L. Stachó[1] and Miklós I. Bán[2]**

[1] Bolyai Institute for Mathematics, Attila József University, Aradi Vértanuk tere 1, H-6720 Szeged, Hungary

[2] Institute of Physical Chemistry, Attila József University, P.O. Box 105, H-6701 Szeged, Hungary

Received April 10, 1991/Accepted January 3, 1992

Summary. The aim of this paper is to give a well-parallelizable curve variational method of finding Fukui's IRC and locating saddle points or other stationary points on potential energy surfaces of chemical reactions, based upon Mezey's theory on catchment regions of the gradient field in mass weighted coordinates.

Key words: Potential energy surface – IRC – Saddle point – Catchment regions

1. Introduction

The most important problem of reaction kinetics of chemical systems is the investigation of reaction mechanisms, especially the course of a chemical reaction described by the reaction path (RP) (see e.g. [2] and references therein). During the past two decades enormous efforts have been devoted to developing theories, theoretical methods, algorithms and computational programs to approximate the experimental RP. It is almost impossible to cite or even to select the most significant papers in this subject. Therefore we will limit our citations to perhaps the best two recently published books [3, 4] in which the reader can find all the references with respect to the concepts to be used in our article and the papers referring to such problems.

The best approach so far still seems to be that obtained by Fukui [5, 6] who introduced the concept of intrinsic reaction coordinate (IRC). The first practical algorithm for calculating IRC was given by Ishida et al. [7]. The IRC can be considered as the union of steepest descent paths, in mass-weighted coordinate systems on the potential energy hypersurface (PHS), connecting the minima of reactants and products, respectively. Nowadays the IRC is regarded by chemists as similar to the minimum energy reaction path (MERP). When studying simple chemical reactions one always finds a saddle point (transition state) on the PHS from which two steepest descent paths lead down, the one to the reactant and the

* A second part of this series will be dealing with applications to relatively simple chemical systems [1] by using semiempirical quantum chemical methods for obtaining the energy functional

** *Correspondence to*: M. I. Bán

other to the product minima. The transition-state theory motivated the development of algorithms locating first, with a very high accuracy, stationary points on the PHS and then issuing steepest descent paths from such points into certain directions of eigenvectors of the Hessian. One of the most popular procedures of this kind, still in use, is that of McIver and Komornicki [8]. When applying this method, some authors (see e.g. [9] and references therein), nevertheless, found the phenomenon of the so-called "chemical hysteresis". Although it may happen that the observed hysteresis is due to the high numerical instability of determining steepest descent paths starting towards a given direction, it can be suspected that the real reason is much deeper. In this paper we shall see in Sect. 2.3 an artificial mathematical PHS where it is impossible to connect two minima with only two steepest descent paths meeting in one point. This result suggests the possibility of the presence of more than one stationary (e.g. saddle-) point along one IRC even for real and elementary chemical reactions. Quite recently, for the conformational changes of the catechol molecule [10] an energy function with such properties was really found. Furthermore, other authors have described interesting chemical examples where the reaction channel bifurcates after the transition state [11], in which case the steepest descent line from the transition state does *not* descend into the catchment basins of *either* one of the two products but rides along the ridge separating the two product basins [12]. These possibilities also imply serious numerical consequences concerning the approaches of McIver and Komornicki types. Their instability may be insupportable and the correction of such instabilities can only be carried out by complicated and tedious procedures. These difficulties called our attention to global curve variational methods.

The aim of the present paper is to suggest a well-parallelizable curve variational method of finding IRC where the initial data may be almost any piecewise analytic curve joining two given local minima. This method is based upon a rigorous mathematical investigation [13] of some aspects of Mezey's theory [14, 15] on catchment regions of the gradient field of U with respect to mass-weighted coordinates. Our main idea is utilizing the observation that starting from an almost arbitrary path connecting two minima, the (nonlinear) shifts of this curve along the negative gradient constitute a path homotopy converging uniformly to some IRC under not too restrictive conditions. To show the effectiveness and reliability of our method, in this paper only the outlines of the mathematical background and applications to artificially constructed functions similar in their behavior to the potential of the catechol conformational changes [10] have been given. In Sect. 2 the concise summary of the strategy, the fundamental theorem and the idealized algorithm of principle upon which several numerical methods may be based have been presented. The rigorous mathematical arguments will be described in a separate article [13]. The present paper can be understood without Ref. [13], nevertheless, the latter contains indispensable information on the properties of convergence for those who are interested in the numerical realization of the idealized algorithm for larger systems.

However, here we are going to state but the fundamental theorem in a rigorous mathematical form for the gradient field of a potential function, representing the simplest situation of chemical interest. For the sake of conciseness and theoretically well-manageable formulation, we use the notations of pure mathematics concerning differential operators and vector fields. The footnote[1] below explains them in a self-contained way. For readers familiar with differential

geometry on manifolds it may be clear that the results can be extended to analytic vector fields on analytic manifolds with analogous conditions on the singularities. Moreover, it can be expected that further generalizations to vector fields with singularities of higher order are possible. We sketch in Sect. 2.5 also the main features of a highly parallelizable simple computer program by which the first numerical experiences were gained. Section 3 shows the experiences attained by the procedure on an artifical function which is problematic for most known algorithms, due to the existence of three neighboring saddle points. In a next paper [16] the detailed algorithm of perhaps the simplest numerical implementation of the procedure and a detailed demonstration of the most important features of the algorithm on the sample function of Sect. 3 will be given. In another paper [17] of this series we shall publish the flow-chart and FORTRAN codes of our computer program with a sequence of practical hints.

Using the fundamental theorem in Sect. 2 and the techniques in [16, 17] the procedure will be illustrated on chemical examples in [1].

2. Method

Our main theoretical tool is the following theorem (to be proved in [13] in a sharper form):

2.1. Theorem[1]

Let $f: \mathbb{R}^n \to \mathbb{R}$ be an analytic function such that

(i) the set $S := \{x : Df(x) = 0\}$ of singularities is finite

(ii) every singularity of f is of Siegel type (i.e. if $y \in S$ then $\det D^2 f(y) \neq 0$ and the vector field $-Df(x)\,\partial/\partial x$ is analytically linearizable in some neighbourhood of the point y)

(iii) $f(x)$, $\|Df(x)\| \to \infty$ for $\|x\| \to \infty$.

---

[1] Throughout this paper our mathematical notations will highly conform to the standards of Mezey's monograph [4]. Furthermore, we are using the following conventions, concerning vector fields and differential operators, from pure mathematics (cf. [18]):

$\mathbb{R}^n$ denotes the usual Euclidean n-space of all real n-tuples $x := (x_1, \ldots, x_n)$ equipped with the norm $\|x\| := (\sum_{k=1}^n x_k^2)^{1/2}$.

For a function f of n variables ($f: \mathbb{R}^n \to \mathbb{R}$) the gradient of f at the point x is denoted by $Df(x)$ ($:= \partial f/\partial x_1|_x, \ldots, \partial f/\partial x_n|_x$). Here we are going to use explicitly only the second power of the operator D. We can naturally identify $D^2 f(x)$ with the Hessian matrix $(\partial^2 f/\partial x_j\, \partial x_k|_x)_{j,k=1}^n$.

In accordance with the conventions of modern calculus of analytic vector fields, if a vector field is given on $\mathbb{R}^n$ which assumes the vector $V(p)$ $(= v_1(p), \ldots, v_n(p))$ at the point p then we write formally $V(x)\,\partial/\partial x$ for it. This notation goes back to the fact that calculations in the enveloping algebra of the Lie algebra of all analytic vector fields can be carried out with this symbolism in the most elegant way.

From the calculus of analytic vector fields we only need the concept of exponential. This can be defined elementarily as follows. Given a vector field $V(x)\,\partial/\partial x$ and a point z, the path $t \mapsto \exp(tV(x)\,\partial/\partial x)z$ is the maximal solution of the initial value problem $d/dt\, x(t) = V(x(t))$; $x(0) = z$. Thus, to calculate the point $\exp(V(x)\,\partial/\partial x)z$ we have to solve the above differential equation and then the required point equals to $x(1)$ if the maximal solution is defined for $t = 1$. For the connections of the exponential of a linear differential operator and the exponential of the corresponding vector field see e.g. [19].

Then the catchment regions of the points of S cover the whole $\mathbb{R}^n$. Assume $\{c(p) : p \in [0, 1]\}$ is a piecewise analytic curve joining two local minima of f which changes catchment region finitely many times. Then, by writing $\bar{c}^t$ for the curve $\exp(-tDf(x)\,\partial/\partial x)c$ with parametrization proportional to arc length on $[0, 1]$, the curves $\{\bar{c}^t(s) : s \in [0, 1]\}$ converge uniformly on some IRC joining $c(0)$ and $c(1)$ for $t \to \infty$.

2.2. *Remark*

A careful examination of the boundaries of catchment regions (see [13]) shows that the hypothesis of the theorem is very probably satisfied for an arbitrary admissible initial curve. For instance, if we restrict our attention to polygons with a fixed number of vertices joining the two minima, then such a polygon changes, with probability 1, catchment regions finitely many times (with respect to the homogeneous distribution of the vertices).

Concerning the local linearizability of vector fields around stationary points we refer to the famous Hartman–Grobman theorem [18, 20] and its analytic extension by Siegel [21].

2.3. *Example*

Let $f(x_1, x_2) := (x_1^2 - 1)^2(x_1^2 + 1/3) + x_2^2$. Then $S = \{(0, 0), (\pm 1, 0), (\pm 1/3, 0)\}$. The respective catchment regions are $\Delta_{(-1,0)} = \{x : x_1 < -1/3\}$, $\Delta_{(-1/3,0)} = \{x : x_1 = -1/3\}$, $\Delta_{(0,0)} = \{x : |x_1| < 1/3\}$, $\Delta_{(1/3,0)} = \{x : x_1 = 1/3\}$, $\Delta_{(1/3,0)} = \{x : x_1 > 1/3\}$.

Let

$$c(p) := \begin{cases} (-1, 3p) & 0 \leqslant p \leqslant 1/3 \\ (6p - 3, 1) & 1/3 \leqslant p \leqslant 2/3 \\ (1, 3 - 3p) & 2/3 \leqslant p \leqslant 1. \end{cases} \tag{1}$$

Then

$$\{c^t(s) : s \in [0, 1]\} = \{(\pm 1, y) : 0 \leqslant y \leqslant \exp(-2t)\} \cup \{(x, \exp(-2t)) : -1 \leqslant x \leqslant 1\}.$$

Thus, for $t \to \infty$, the curves $\{c^t(s) : s \in [0, 1]\}$ converge to the IRC $\{(x, 0) : -1 \leqslant x \leqslant 1\}$ passing through the three transition states $(-1/3, 0)$, $(0, 0)$, $(1/3, 0)$. However, there is obviously no other IRC connecting the minima $(-1, 0)$, $(1, 0)$.

Theorem 2.1 suggests the following numerical approach:

2.4. *Idealized algorithm*

Initial data: an analytical function $f : \mathbb{R}^n \to \mathbb{R}$ and a piecewise analytic curve $c : [0, 1] \to \mathbb{R}^n$ joining two minima of f.

Step 1). Determine the solution of:

$$\frac{d}{dt} c^t(p) = -Df(c^t(p)) \qquad c^0(p) = c(p) \tag{2}$$

for every $p \in [0, 1]$.

Step 2). Reparametrize each curve $\{c^t(p) : p \in [0, 1]\}$ on $[0, 1]$ proportionally to arc length. Hence we obtain the new parametrizations:

$$C^t\left(\frac{\text{length}\{c^t(p) : p \in [0, r]\}}{\text{length}\{c^t(p) : p \in [0, 1]\}}\right) := c^t(r) \quad (r \in [0, 1],\ t \geq 0). \tag{3}$$

Step 3). Take the limits $I(r) := \lim_{t \to \infty} C^t(r)$ for every $r \in [0, 1]$. The curve I is an IRC such that $I(0) = c(0)$ and $I(1) = c(1)$. The convergence is uniform if f and c fulfill the hypothesis of Theorem 2.1.

2.5. Numerical methods for determining IRC of the adiabatic potential energy U

It is well known that the function U is bounded and $\|DU(x)\| \to 0$ for $\|x\| \to \infty$. Thus we must consider some perturbed function $f := U + g$ where g and its derivatives are small inside a domain where the IRC is expected and $g(x)$, $\|Dg(x)\| \to \infty$ as $\|x\| \to \infty$. For instance, it may be convenient to choose g in the form $g(x) := \|x/R\|^N$ for some large radius R and power N. However, it seems that for most practical cases such a perturbation is unnecessary although some technical assumptions of Sect. 2.1 are not satisfied. Even by using a perturbation, it may happen that, for reasons of symmetry, some singular points are not hyperbolic. Most such cases can be managed by restricting ourselves to a smaller number of new intrinsic coordinates invariant with respect to the symmetries in question.

Instead of imitating the steps of Sect. 2.3 (by applying appropriate numerical methods of carrying them out in discrete values), the following treatment is suggested.

Besides f and c we need three parameters $t_0, \varepsilon, \delta > 0$ (to be fixed appropriately) for controlling the procedure. For every $x \in \mathbb{R}^n$ let $\phi(x)$ denote an approximate value of the solution of $d/dt\, z(t) = -Df(z(t))$; $z(0) = x$ for time $t = t_0$. For $l = 0, 1, \ldots,$ in Step l) we determine a finite sequence $c_1, \ldots, c_N \in \mathbb{R}^n$ of points approximating the points $C^t(\varepsilon/S^t), C^t(2\varepsilon/S^t), \ldots, C^t([S^t/\varepsilon]\varepsilon S^t)$ for $t := lt_0$ where $S^t := \text{length}\{C^t(t) : r \in [0, 1]\}$ of the curve C^t in Sect. 2.3.

Step 0). Choose $p_0, \ldots, p_N$ so that $p_0 = 0$, $p_N = 1$ and, by setting $c_k := c(p_k)$ we have $\|c_{k-1} - c_k\| \leq \varepsilon$ for $k = 1, \ldots, N$.

Suppose we have constructed $c_0, \ldots, c_N$ in Step l).

Step $l + 1$). Determine $c'_k := \phi(c_k)$ $(k = 0, \ldots, N)$. Note that $c'_0 = c_0 = c(0)$ and $c'_N = c_N = c(1)$. Determine points $c''_1, c''_2, \ldots, c''_M$ on the polygon with consecutive vertices $c'_0, \ldots, c'_N$ such that $c''_0 = c'_0$, $c''_M = c'_N$ and $\|c''_{k-1} - c''_k\| \leq \varepsilon$ $(k = 1, \ldots, M)$. Store M in N and set $c_k := c''_k$ $(k = 1, \ldots, N$ with the new value of $N)$.

STOP condition). Finish the procedure by declaring that the polygon with consecutive vertices $c_0, \ldots, c_N$ is an approximating IRC if:

$$\arccos\left(\sum_{i=1}^{n} (c_{k+1} - c_{k-1})i \frac{\partial}{\partial x_i} f(c_k) / \|c_{k+1} - c_{k-1}\|\right) \leq \delta \quad (k = 1, \ldots, N-1).$$

3. Numerical experiences

Theorem 2.1 and the results given in [13] in a more detailed and general fashion ensure that the method in Sect. 2.5 is suitable in computing IRC with arbitrary

accuracy when choosing sufficiently small the governing parameters t_0, ε and the accuracy of the approximating solution ϕ. However, it seems to be difficult to give good estimates for the rate of convergence in terms of the mentioned parameters along the lines described in [13].

3.1. Experimental algorithm

We used a version of the method in Sect. 2.5 where the approximating polygon $C^{l+1} = \{c_0'', \ldots, c_M''\}$ for the $(l+1)$th step is constructed from the approximating polygon $C^l = \{c_0, \ldots, c_N\}$ of step l as follows. For $k = 1, \ldots, N$ we add $[\|c_k' - c_{k-1}'\|/\varepsilon] - 1$ points to C^l which partition equidistantly the segment between $c_k' := \phi(c_k)$ and $c_{k-1}' := \phi(c_{k-1})$. Then we relax a maximal subset of the obtained polygon such that the consecutive vertices of the remainder polygon C^{l+1} lie in a distance not greater than ε from each other. For the approximation ϕ of $\exp[t_0 Df(x)\,\partial/\partial x]$ we used K gradient steps of time t_0/K with variable step number K. In this manner we could also make simple experiments with methods of various accuracy by changing the parameter K.

3.2. Sample functions and curves

First we applied the above-described version of the method in Sect. 2.5 to functions of the form:

$$f(x) = \sum_{j,k=1}^{10} a_{jk} x_1^j x_2^k \quad (x \in \mathbb{R}^2) \tag{4}$$

with singularities lying in the square $[0, 1]^2$ (i.e. $S \subset \{(x, y) : |x|, |y| \leqslant 1\}$). Initial curves were always located in the square $[1.2, 1.2]^2$ and the gradient vectors of f on the boundary of $[1.2, 1.2]^2$ were directed outward from the square and their norms did not exceed the value 300.

3.3. Experiments

Instead of letting run the procedure until satisfying the STOP condition we plotted the resulting curve after each step and we stopped the procedure manually.

3.4. Experiences

In each case a choice of $\varepsilon \leqslant 0.2$ was sufficient for the fineness of the curves in giving a satisfactory IRC approximation. However, we always used functions that we could control easily by manual calculations and these functions admitted IRCs consisting of almost not winding pieces.

It is advisable to choose t_0 small so that the mapping ϕ take two points lying in a distance less than ε into a couple with distance less than 3ε. (Otherwise some strange oscillations may occur.) It is also advisable that the imaginary time t_0/K of one gradient step should be small so that we have $(t_0/K)\,\|Df(x)\| < \varepsilon$ whenever the point x lies in the stable domain (e.g. in our case in $[1.2, 1.2]^2$).

3.5. *Example*

Consider the function:

$$f(x) := \prod_{j,k=0,1} \|x - ((-1)^j, (-1)^k)\|^2 + (x_1^2 - 1)^3 - (x_2^2 - 1)^3. \tag{5}$$

This admits local minima at the points $(\pm 1, \pm 1)$, a saddle point at $(0, 0)$ and two further saddle points with coordinates $(0, \pm 0.37213)$. Notice that $f \geqslant 0$ and the critical values are $f(\pm 1, \pm 1) = 0, f(0, 0) = 16, f(0, \pm 0.37213) = 15.793215$. We shall see that any IRC joining the minima $(-1, 1)$ and $(-1, -1)$ or the minima $(-1, 1)$ and $(1, -1)$ should pass through all the three saddle points of f.

We show in three instructive cases how the curves develop in the consecutive steps in Sect. 3.1 with parameters $\varepsilon := 0.15$, $t_0 := 0.01$, $K := 250$.

Case 1). Starting curve: $c^0 : [0, 1] \ni t \mapsto (-1, 2t - 1)$. We display in Fig. 2a the curves c^0, $c^{0.01}$, $c^{0.03}$, $c^{0.09}$, $c^{0.27}$, $c^{1.07}$. Dots indicate the representing points given by the procedure and they are linearly interpolated on each curve.

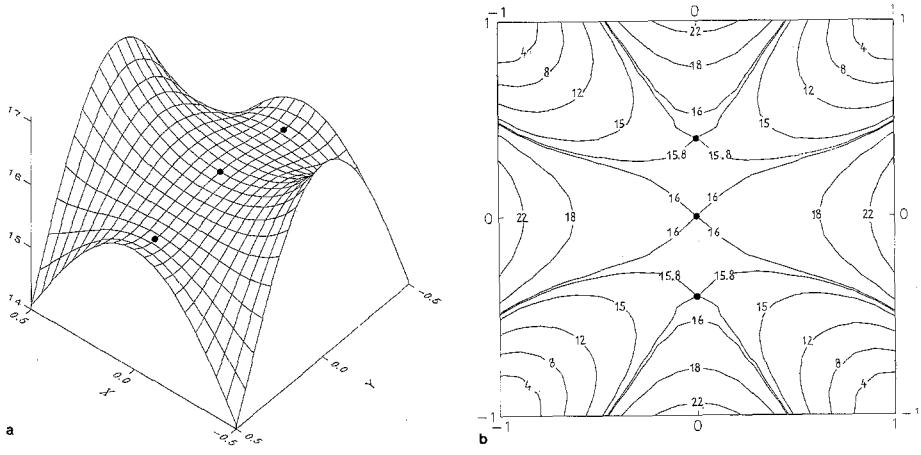

Fig. 1. **a** Saddle points of f. **b** Level set of f

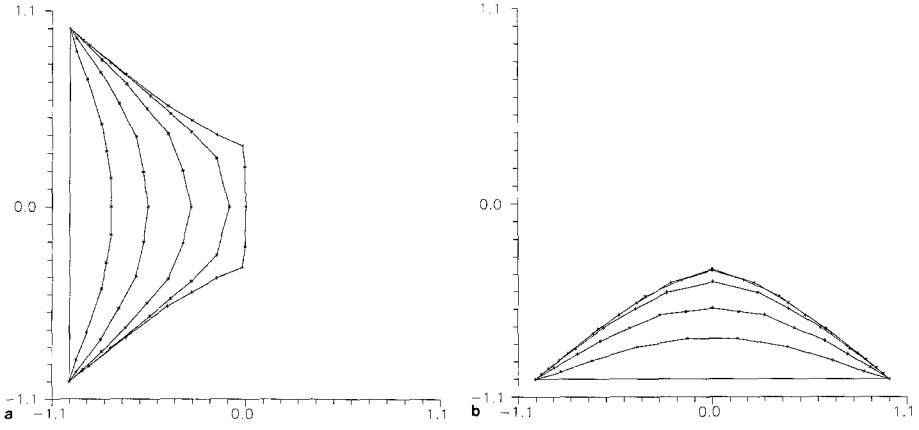

Fig. 2. **a** Curves in Case 1). **b** Curves in Case 2)

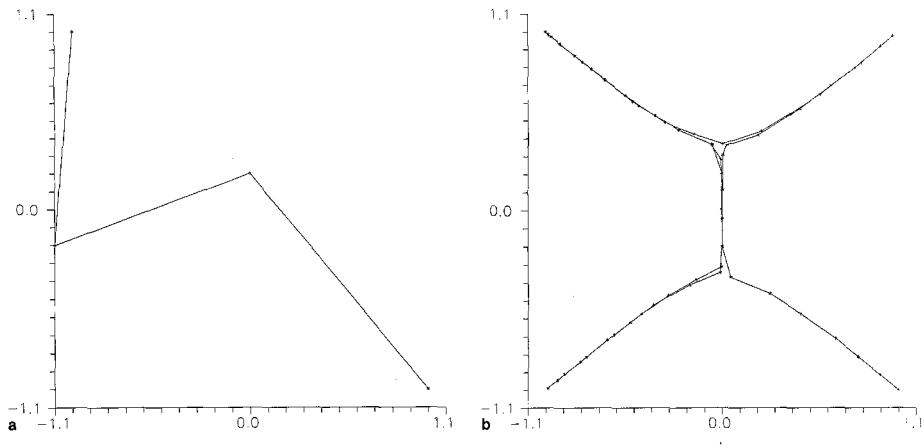

Fig. 3. **a** Initial curve in Case 3). **b** Final curve in Case 3)

Case 2). Starting curve: $c^0:[0, 1] \ni t \mapsto (2t-1, -1)$. We display in Fig. 2b again the curves c^0, $c^{0.01}$, $c^{0.03}$, $c^{0.09}$, $c^{0.27}$, $c^{1.07}$. The convergence in this region is faster. The coincidence of $c^{0.27}$ with $c^{1.07}$ is remarkable.

Case 3). Now we choose a more complicated starting curve intersecting all the catchment regions. Let c^0 be the polygon in Fig. 3a joining the points $(-1, 1)$, $(-1.1, -0.2)$, $(0, 0.2)$, $(1, -1)$. The resulting IRC of "form H" in Fig. 3b joining the minima $(-1, 1)$ and $(1, -1)$ wanders through all possible IRC pieces contained in $[0, 1]^2$ of the graph surface of f.

References

1. Dömötör Gy, Körtvélyesi T, Stachó LL, Bán MI (in preparation) Theoret Chim Acta
2. (a) Bálint I, Bán MI (1983) Theoret Chim Acta 63:255; (b) Bálint I, Bán MI (1984) Int J Quantum Chem 25:655
3. Jørgensen P, Simons J (1985) Geometrical derivatives of energy surfaces and molecular properties. Reidel, Dordrecht
4. Mezey PG (1987) Potential energy hypersurfaces. Elsevier, Amsterdam
5. Fukui K (1970) J Phys Chem 74:4161
6. Tachibana A, Fukui K (1978) Theoret Chim Acta 49:321
7. Ishida K, Morokuma K, Komornicki A (1977) J Chem Phys 66:2153
8. McIver JW, Komornicki A (1974) J Am Chem Soc 96:5798
9. Bálint I, Bán MI (1983) Int J Quantum Chem 24:161
10. Mezey PG (1990) J Am Chem Soc 112:3791
11. Xantheas S, Elbert ST, Ruedenberg K (1991) Theor Chim Acta 78:365
12. Valtazanos P, Ruedenberg K (1986) Theor Chim Acta 69:281
13. Stachó LL, Bán MI (in press) J Math Chem
14. Mezey PG (1981) Theoret Chim Acta 58:309
15. Mezey PG (1982) Theoret Chim Acta 62:133
16. Stachó LL, Bán MI (submitted) Theoret Chim Acta
17. Stachó LL, Bán MI (submitted) Computers Chem
18. Guckenheimer J, Holmes Ph (1986) Nonlinear oscillations, dynamical systems and bifurcations of vector fields. Applied Math Sci. Vol 42, Springer, NY
19. Isidro JM, Stachó LL (1985) Holomorphic automorphism groups in banach spaces. North-Holland Math Studies, Vol 105. Elsevier, Amsterdam
20. Palis J, de Melo W (1980) Geometric theory of dynamical systems. Springer, NY
21. Siegel CL (1952) Nachr der Acad Wiss Göttingen, p 21