

## ABOUT A CERTAIN DYNAMICAL SYSTEM IN MOLECULAR CONFIGURATION SPACE

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### ABSTRACT

As an example of dynamical system, glycine has been calculated through the molecular mechanics approach. Of the three planar conformations studied, only one equilibrium points region could be considered as a catchment region. On the other hand, an intriguing relation appears between the gradient norm and the spectral radius of the matrix representing the metric tensor.

Keywords: Dynamical system - Gradient norm and metric tensor

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## 1. INTRODUCTION

We started this work having in mind the study of a dynamical system [1]. As an example of an energy-minimized, geometry-optimized molecular system we chose glycine, for which we also made a seek for catchment regions [2]. The corresponding calculations have been performed using the molecular mechanics (MM) method [3]. We have studied the three most usual planar conformations; we show more in detail the one exhibiting the greatest diversity in the features of the dynamical system solutions.

We have followed the spectral radius of the metric tensor, along several of these solutions. We have then gathered in a table the spectral radii obtained in the final points as well as the corresponding gradient norms. Unexpectedly, a relation seems to link these two quantities.

## 2. MANIFOLDS, DYNAMICAL SYSTEMS AND CATCHMENT REGIONS

We denote by  $R^n$  the set of all  $n$ -tuples of real numbers  $(x_1, x_2, \dots, x_n)$ , i.e. the usual  $n$ -dimensional space of vector algebra. A set (of "points")  $M$  is defined to be a manifold if each point  $P$  of  $M$  has an open neighbourhood which has a homeomorphism  $f$  onto an open set of  $R^n$  for some  $n$  (see Fig. 1). An homeomorphism is a continuous 1-1 map from one space to another, having a continuous inverse. Thus,  $M$  is locally "like"  $R^n$ [3]. The map is not required to preserve lengths or angles.

Let us now see dynamical phenomena which may be described as taking place within a manifold [4]. If the function  $E: U \rightarrow R$  is defined in the open set  $U \subset R^n$ , its gradient  $\nabla E: U \rightarrow R^n$  is a vector  $x$  of components

$$x \mid \rightarrow (\partial E / \partial x_1, \dots, \partial E / \partial x_n) \quad (1)$$

The gradient points at the direction along which function  $E$  increases most steeply.

A dynamical system in an open set  $U$  is defined by the differential equation

$$\dot{x} = f(x) ; f: U \rightarrow R^n \quad (2)$$

For a gradient system

$$\dot{f}(x) = -\nabla E(x), \quad (3)$$

where  $E$  is the system's energy.

The points where  $\nabla E = 0$  are called equilibrium points. The equilibrium points of (2) are classified following the behaviour of the solutions in its neighbourhood and the notion of stability given here is that attributed to Liapunov [4].

We shall say that an equilibrium point  $x_s$  is stable, if for every neighbourhood  $V$  of  $x_s$  there exists a neighbourhood  $W$  of  $x_s$ ,  $W \subset V$ , where any solution of (2)  $x(\lambda)$  with  $x(0)$  in  $W$  remains within  $V$  for any  $\lambda > 0$  (Fig. 2a).

An equilibrium point  $x_s$  is asymptotically stable if, besides being stable, any solution  $x(\lambda)$  of (2) with  $x(0)$  within  $W$  converges to  $x_s$  (Fig. 2b). Finally, an equilibrium point  $x_u$  is unstable if there exists a neighbourhood  $V$  of it such that, for any neighbourhood  $W$  of  $x_u$ ,  $W \subset V$ , at least one solution  $x(\lambda)$  of (2) having  $x(0)$  within  $W$  does not remain within  $V$  for any  $\lambda > 0$  (Fig. 2c). Furthermore, if  $x$  is an isolated minimum of  $E$ ,  $x$  is an asymptotically stable point of (2) [4].

The energy along the solutions of (2) is non-increasing. These solutions are known as steepest descent paths [5,6]. The internal coordinates of an  $N$ -atoms molecular system define a  $(3N-6)$  configuration space, which is a manifold of class  $C^\infty$ . The gradient system, of course, may be described in terms of configuration space.

The well known works of Fukui and Tachibana [7] apply some of the above mentioned concepts from the theory of dynamical systems to chemical reactions.

Stable and transition structures are, respectively, asymptotically stable equilibrium points and unstable equilibrium points of the system. For asymptotically stable equilibrium points  $x_s$  we shall take all the solutions of (2) tending to  $x_s$  and for unstable equilibrium

points  $x_u$  we take the solutions of the system tending to  $x_u$ , if they exist (Fig.3). The range of possible distortions of a molecular conformation which preserve chemical identity is known under the name of catchment region [1,8].

Now, a theorem discussed by Pechukas [5] states that every point belonging to a solution of a gradient system preserves the point symmetry group of the starting point. As a corollary of this theorem, nowhere along the solution may a new symmetry element not present in the starting point arise; this can only occur in equilibrium points. Therefore, an equilibrium point corresponds to a conformation having the highest order point symmetry group within its catchment region.

If we analyse any solution within a catchment region, the order of the point symmetry groups of its elements is constant; it could increase only at an equilibrium point. This possibility may direct the search of equilibrium points. Although the study of catchment regions would require mass-scaled coordinates, they are impractical, so conventional internal coordinates will do [8].

Most familiar vector algebras involve an inner product between vectors (scalar product). The metric tensor on an n-dimensional basis  $\{ e_i \}$  has components

$$g_{ij} = e_i \cdot e_j \quad (4)$$

These components form an  $n \times n$  symmetric matrix. This matrix is demanded to have an inverse, of components denoted by  $g^{ij}$  [3]. In this work we shall not be concerned with the most important role of the metric tensor, namely that it maps vectors into one-forms in a 1-1 manner [1] (otherwise stated, it allows to raise or lower, respectively, covariant and contravariant tensor indices [9]). If the basis is orthonormalized, the metric tensor reduces to identity, the unit matrix.

### 3. APPLICATION TO GLYCINE

Glycine, the smallest amino acid, has been subject of extensive theoretical and experimental studies [ 10-16]. Although we have also calculated some of the non-planar possible conformations, we restrict ourselves here to the three most usual planar conformations of glycine under neutral form, shown in Fig.4. The most sophisticated theoretical results agree in appointing conformation I as the most stable one; however, experimental difficulties have prevented verifying this prediction [10,13] and the relative stability of other conformers is still a highly controversial issue [14-16] .

We have used Csázár's [15] internal coordinates as starting parameters in the MM-THOR package used [17]; the program allows options generating energy surfaces and energy contour lines. In order to obtain the results shown in this work, we were led to decrease the grid step of the original program from  $10^{-2}$  to  $10^{-10}$ . The gradient norm, accordingly, is considered zero when attaining  $10^{-10}$ .

We report in Table 1 the relative energies obtained for each conformation. It is seen that before geometry optimization, conformation I appears as the most stable one, while optimization favours conformation III. Nevertheless, the difference between I and III being then only 0.14 kcal/mol, it can hardly be considered meaningful. Glycine appears thus to be an essentially flexible molecule [18], this feature accounting for the unsettled discussion about conformers stability.

Figure 5 shows the energy surface of conformation II as a function of the torsion angles  $\tau(N_4C_1C_2O_3)$  (which we denote N) and  $\tau(O_5C_2C_1O_3)$ , denoted O. Fig. 6 shows the corresponding contour energy lines of this smooth and shallow surface. In the illustrations of conformation I (not shown here), we also find a huge number of equilibrium points. As happens in much more sophisticated calculations, the sensitivity to small energy variations is low. In Ref.[19] different calculation methods are compared when studying glycine energy surfaces; the conclusion is that reproducing such small

energy differences is a challenge for computational chemistry. More recent works [14,15] add uncertainty rather than settle the question.

Turning back to Fig.6, we call  $N_2$  the region of equilibrium points around conformation II. For conformation I there are solutions converging and others diverging from the corresponding region  $N_1$  (not shown here), where N and/or O differ from  $180^\circ$ .  $N_1$  is hence an instability region; since conformation I belongs to it, shares this feature. Császár [15] suggests that the repulsion of lone electron pairs on the N and O atoms may destabilize some glycine planar forms, leading to saddle points. The instability of region  $N_2$  is more accentuated than that of  $N_1$ , due to the two wide regions with lowest energy corresponding to non-planar conformations (see Figs. 5 and 6). As in  $N_1$ , we find in  $N_2$  the symmetry group of planar conformations, of higher order symmetry.

Similarly, Fig.7 shows the equilibrium points region  $N_3$ . All solutions near  $N_3$  not only remain near it, but within the region after a certain time, characterizing thus asymptotically stable equilibrium. Conformation III may hence be considered as such, agreeing with Refs.[12] and [13]. Now it is clearer that the equilibrium point is one of the conformations having the highest order symmetry group within its catchment region; as conformation III is an equilibrium point within  $N_3$  and it exhibits the highest order symmetry element (planar symmetry),  $N_3$  may be considered a catchment region.

#### 4.FURTHER DEVELOPMENTS

We may wonder what happens with a molecule's metric along solutions of a dynamical system such as those in Fig.6. The classical Chirgwin and Coulson work [20] mentions a noteworthy point which has been since then overlooked for many years, namely, that the well known overlap matrix  $S$  of molecular calculations is the metric tensor of the Hilbert space defined by the basis of atomic orbitals. It may be considered as an operator, for it rules the raising or lowering of tensor indices [9]. So, if we desire to

follow the metric behaviour along a given solution, we must choose some quantity related to the overlap matrix. We have opted for the spectral radius, i.e. the highest eigenvalue of  $S$ . This is a possible definition of norm [21]; we shall however speak of spectral radius of tensor  $S$  so as to avoid confusion with the much more familiar definition of norm as a vector's modulus, which we shall employ too.

We use the overlap matrix built from Slater-type orbitals, such as given by the CNDO/2 program [22], of which we have calculated the eigenvalues. Although CNDO supposes Complete Neglect of Differential Overlap, the overlap matrix is used (and it appears in standard output) in the parameterization of the Hamiltonian matrix elements.

Of the three conformations studied, we shall at this stage focus our attention on conformation II, because it shows the greatest range of variation in the characteristics of the dynamical system solutions. We report in Table 2 the behaviour of the spectral radius  $\|S_{ij}\|$  along some points of solution O in Fig.6. Now, in this Table  $\|S_{ij}\|$  decreases along the solution. This is not a general trend. It tends to decrease in solutions A, J, O and X, while it tends to increase for E, F, K, N, S and T. We have found no association between these behaviours and any other quantity. Let us remind that  $\|S_{ij}\|$  measures the maximum stretch which the vectors of unitary radius may undergo upon application of the  $S$  operator [5].

Let us look for a connection between the dynamical system solutions and the gradient norm in the final point of each solution, calculated with the PM3 Hamiltonian of the MOPAC package [23]. The norms  $\|\nabla E\|$  thus estimated have high values because they are calculated with geometries optimized through a completely different method. Let us see first the  $\|\nabla E\|$  results for the three conformations studied; they are respectively 80.0562 (conf. I), 90.3208 (conf. II) and 77.7704 (conf. III). Although the differences in the relative norms is small, they indicate (in agreement with Table 1) conformation III as the most stable one.

We have collected in Table 3 both  $\|\nabla E\|$  and  $\|S_{ij}\|$  for the solutions final points displayed in Fig.6. The Table strongly suggests a link between the two quantities,

although deriving from different programs which share the feature of the indirect use they make of overlap. The overlap integrals are not programmed in the same way in CNDO [22] and in MOPAC [23]; however, for first row atoms they cannot differ appreciably, so that the above mentioned relation should actually apply. Figure 8 shows  $\ln \|\nabla E\|$  plotted against  $\|S_{ij}\|$ . A least-squares calculations yields

$$\ln \|\nabla E\| = 4.447 \|S_{ij}\| - 6.238 \quad (5)$$

with a linear regression coefficient of 0.9705.

Equation (5) furnishes us a relation between  $\|\nabla E\|$  calculated by MM and that given by MOPAC. Let us see why. At first sight, it does not look as consistent with the fact that, when  $\|\nabla E\|$  is zero, its logarithm is  $-\infty$ . Nevertheless, it must be kept in mind that the lower bound to  $\|S_{ij}\|$  is one. This is for strictly orthogonal bases, and bases are never really orthogonal; MOPAC supposes orthogonal bases in all electronic integrals, despite S is used in the Hamiltonian parameterization. For  $\|S_{ij}\| = 1$ , eq. (4) gives

$\ln \|\nabla E\| = -1.791$ , so that  $\|\nabla E\| = 0.167$ , which is thus a shift in the MM-MOPAC scale.

The relation between  $\|\nabla E\|$  and  $\|S_{ij}\|$  given by eq. (5) is entirely unexpected and, of course, it must be taken as a preliminary result, subject to further test.

## 5. CONCLUDING REMARKS

Mezey [8] states a theorem interrelating catchment regions and point symmetries of nuclear configurations. Let us quote what concerns us: "The distribution of catchment regions and their critical points are thus properties of the potential energy surface, that is, they depend on *energy relations*, whereas the point symmetry of various nuclear configurations are purely *geometrical properties*, not directly dependent on energy. Consequently, *the theorem interrelates two very different molecular properties*".



This is exactly the kind of result we have found, a link between the norm of the gradient (a quantity belonging to the energy domain) and the spectral radius of the overlap matrix (a typically geometrical quantity).

### Figure captions

Figure 1. Definition of a manifold.

Figure 2. (a) Stable, (b) asymptotically stable and (c) unstable equilibrium points.

Figure 3. Sets of solutions tending to a certain equilibrium point:  $x_s$ , asymptotically stable;  $x_u$ , unstable.

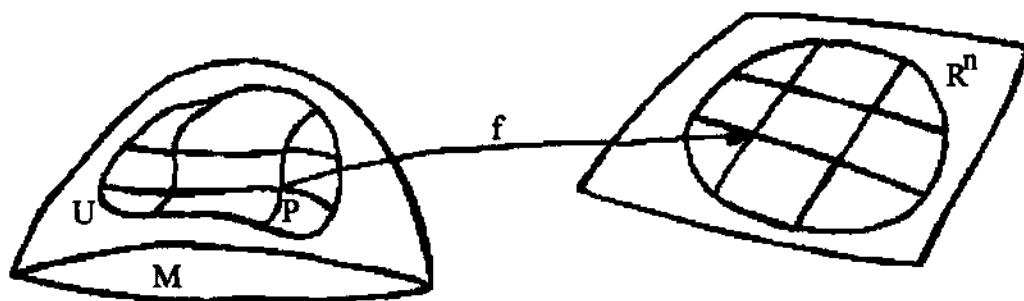
Figure 4. The three most usual planar conformations of neutral glycine.

Figure 5. Energy surface of conformation II as a function of the torsion angles  $\tau(N_4C_1C_2O_3)$  (denoted N) and  $\tau(O_5C_2C_1O_3)$  (denoted O). The energy  $E$  units are kcal/mol.

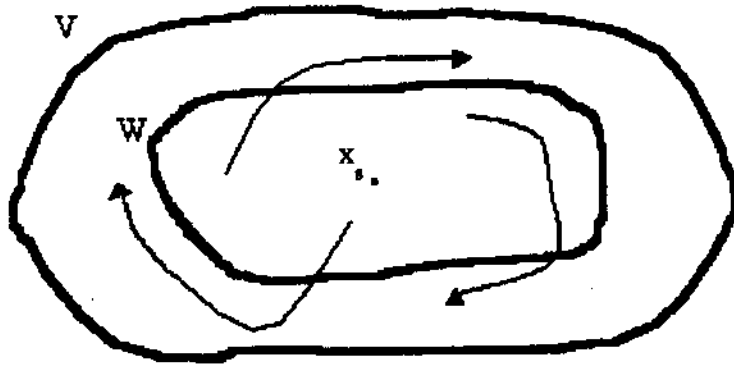
Figure 6. Contour energy lines of conformation II.

Figure 7. Contour energy lines of conformation III.

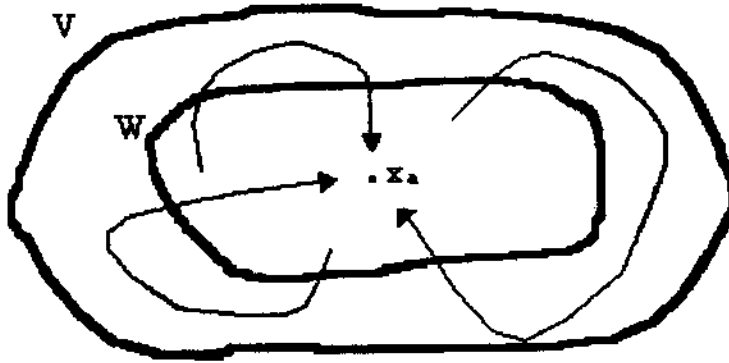
Figure 8. Gradient norm logarithm ( $\ln \|\nabla E\|$ ) as a function of spectral radius  $\|S_{ij}\|$ , both from Table 3.

**Figure 1.**

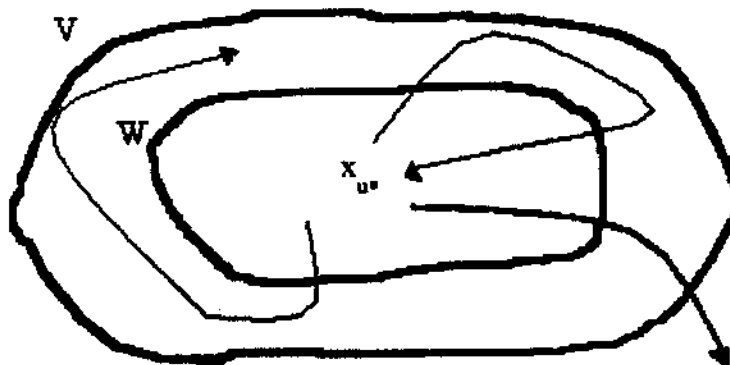
-11-



(a)



(b)



(c)

Figure 2.

-12-

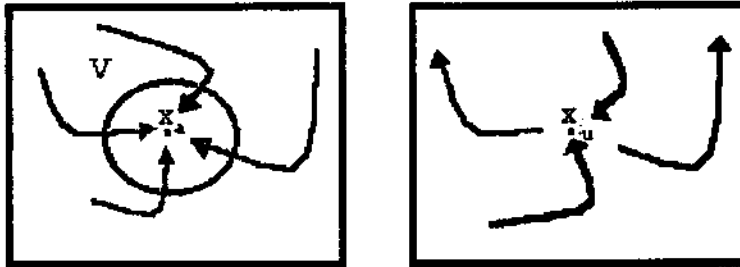


Figure 3.

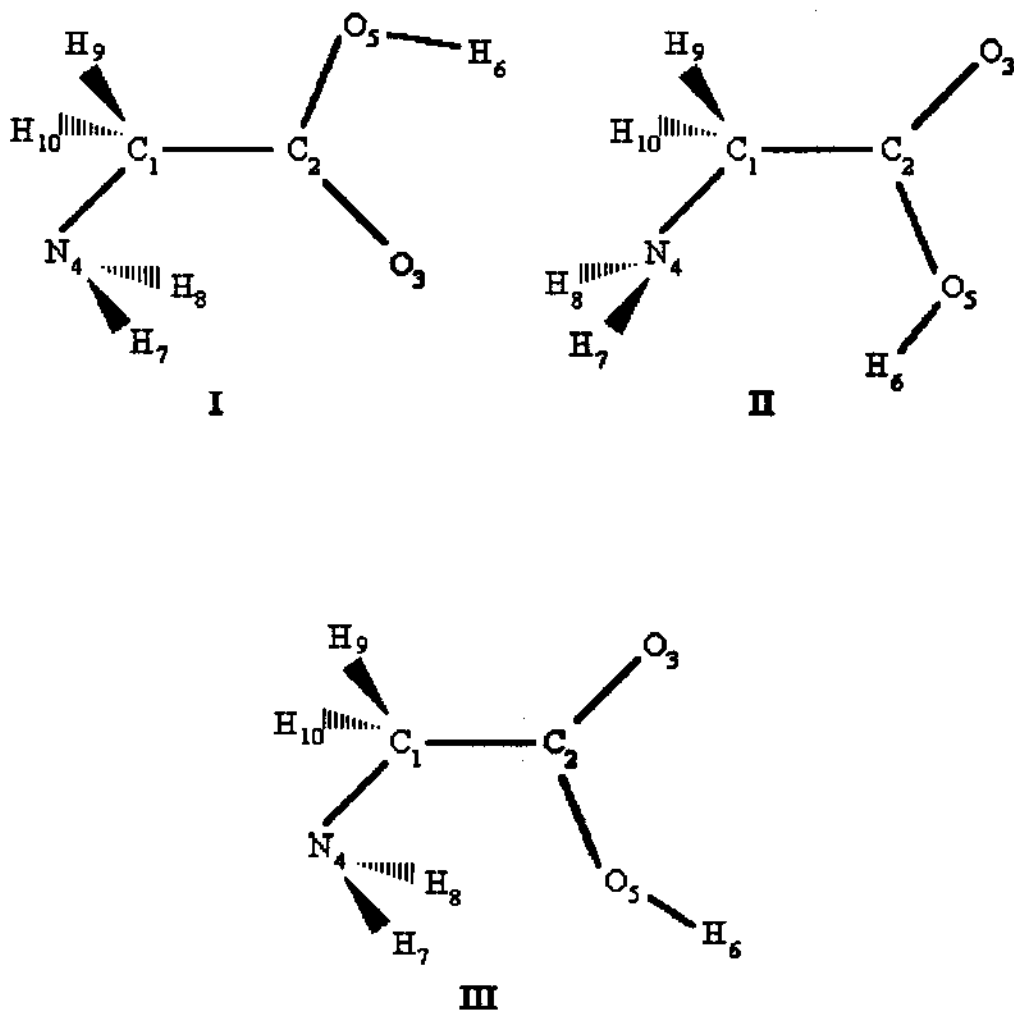


Figure 4.

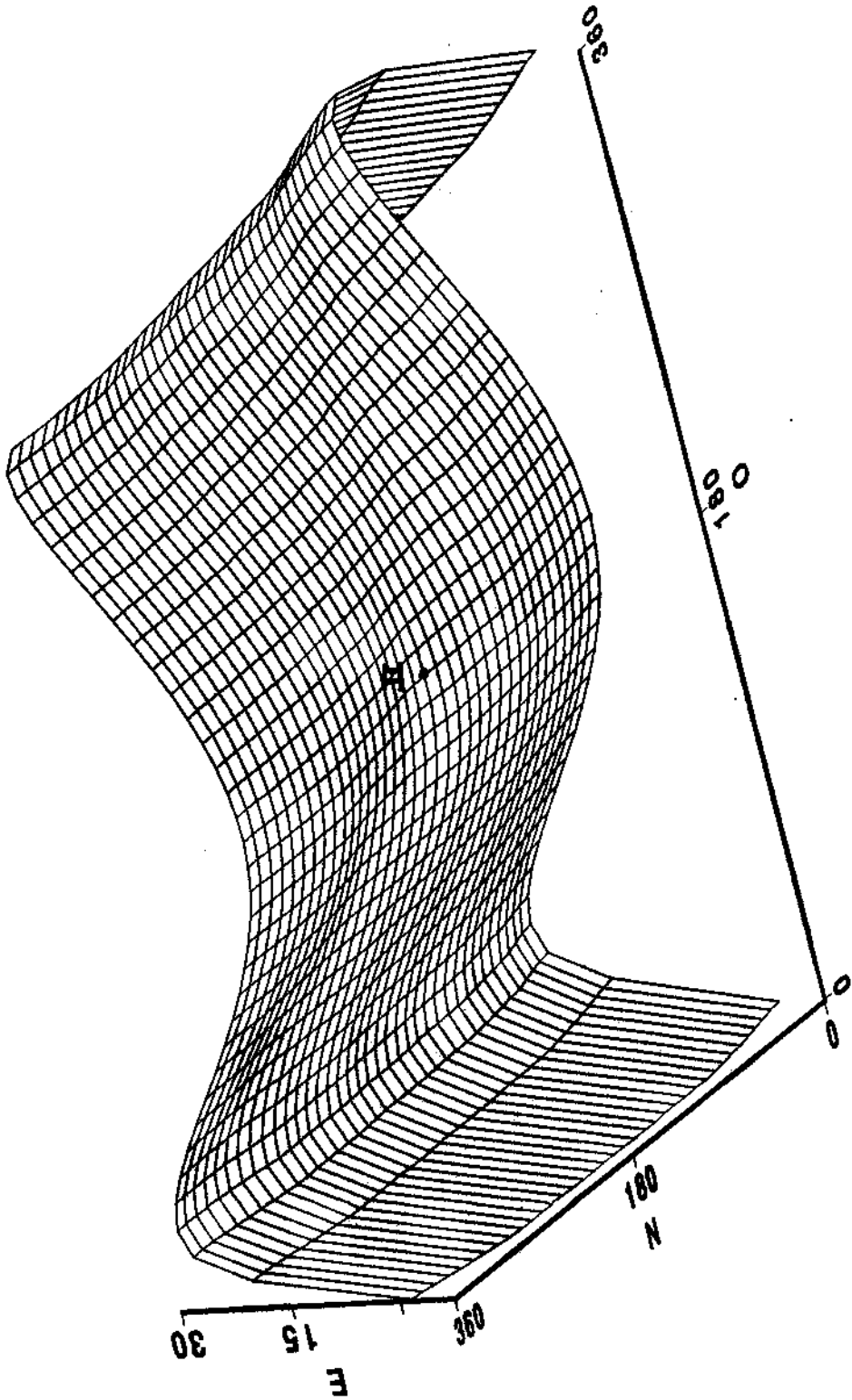


Figure 5.

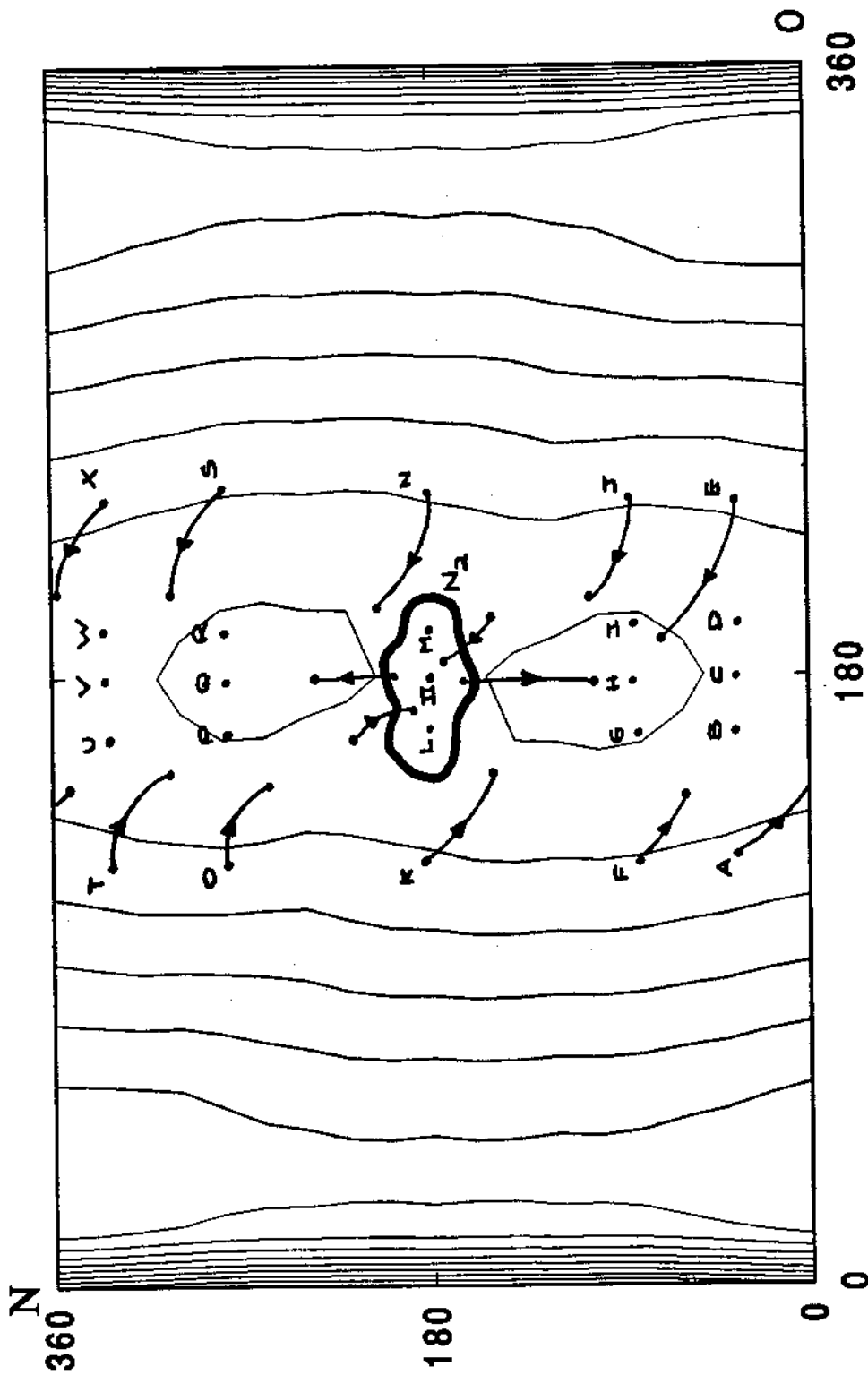


Figure 6.



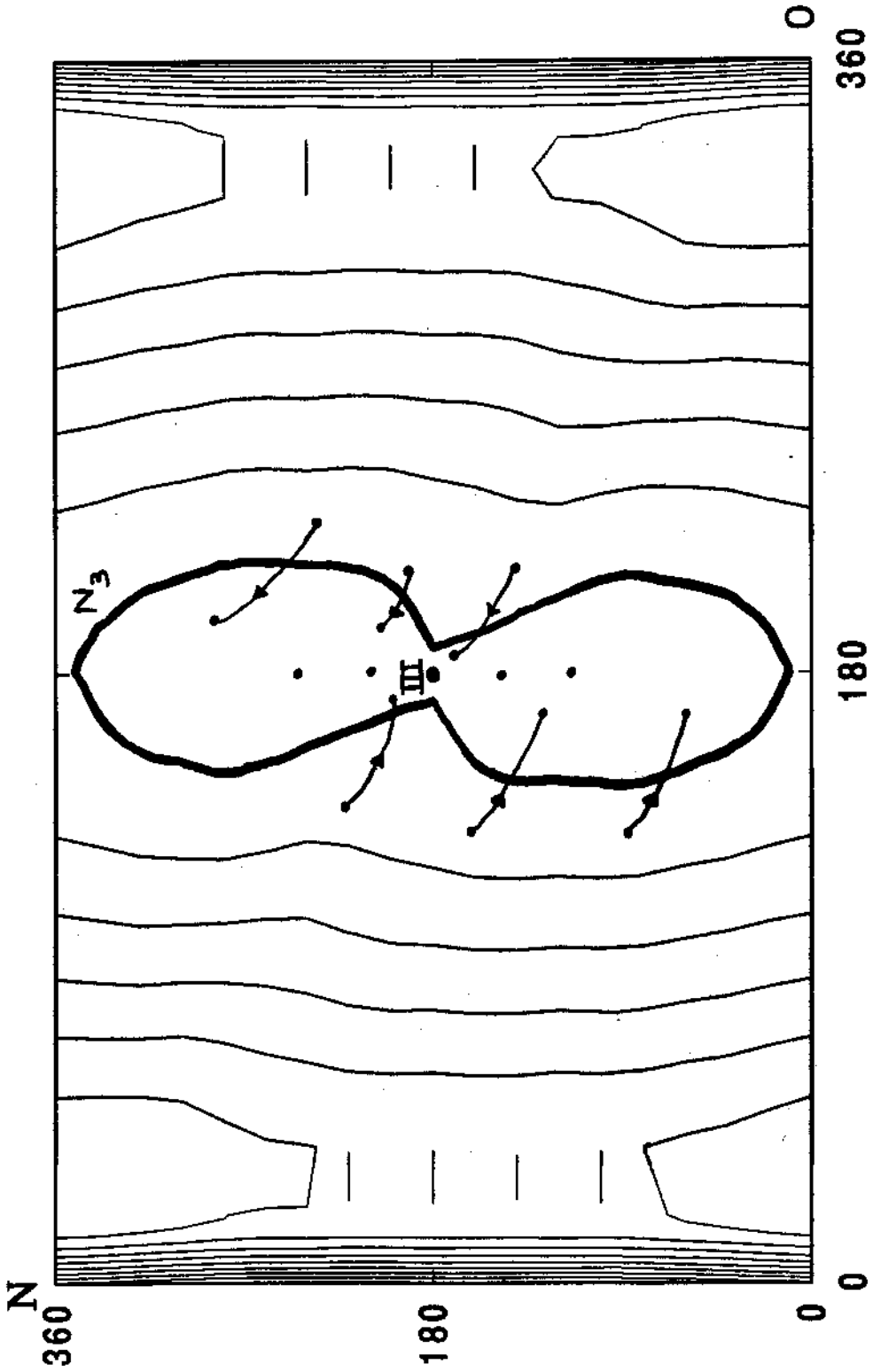


Figure 7.

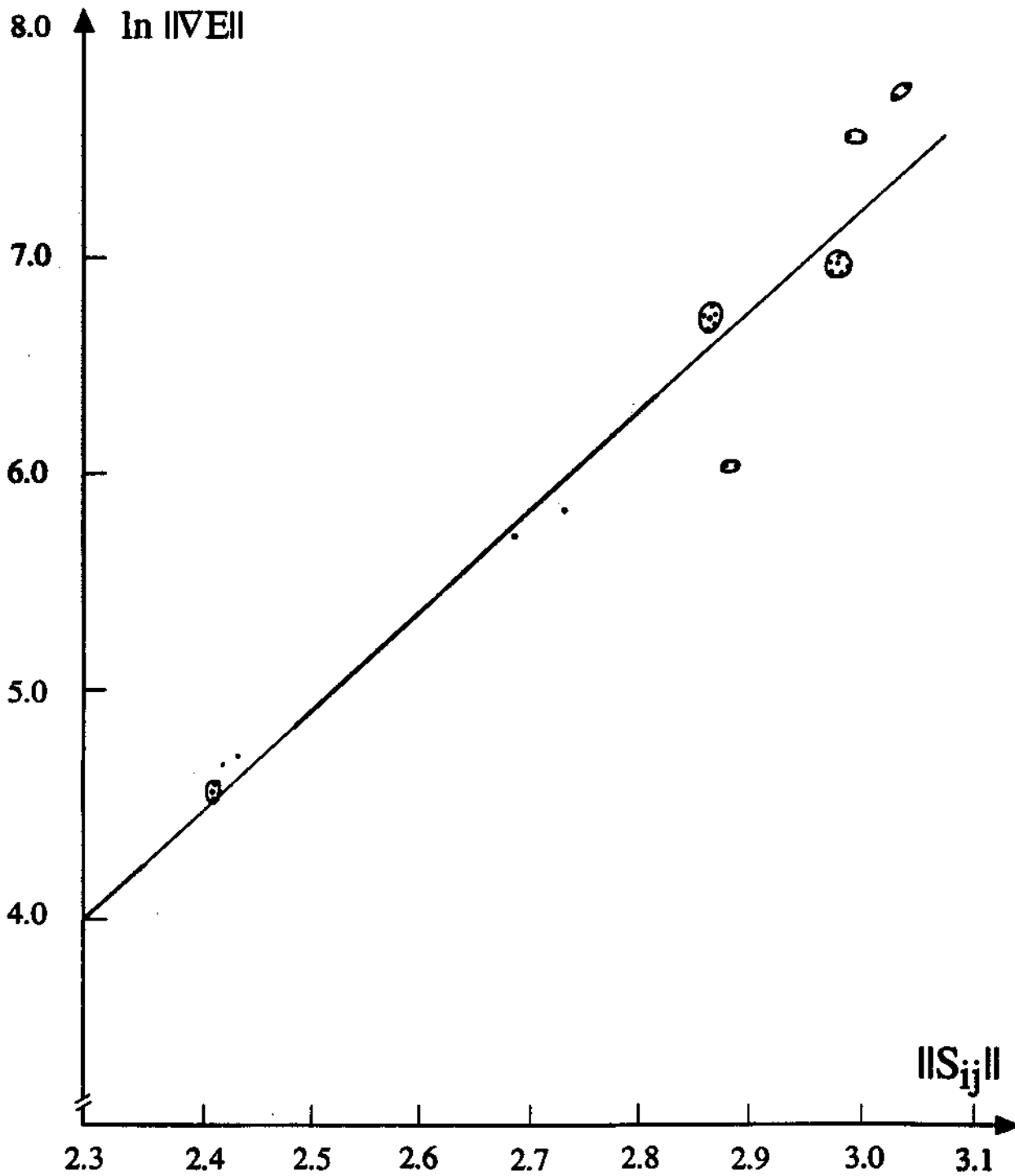


FIGURE 8.

Conf.	I	II	III
E (before opt.)	3.7367	0.000	3.2021
E (after opt.)	14.0893	12.3869	14.2282

Table 1.

Relative energies E of conformations I, II and III (in -kcal/mol) before and after geometry optimization.

N	O	$\ S_{ij}\ $
270	120	2.895
268.65	126.38	2.880
268.44	127.55	2.875
267.93	129.11	2.869
267.53	130.63	2.868
266.55	132.91	2.854
265.76	134.94	2.853
264.13	138.26	2.831
262.87	141.04	2.828
260.41	145.81	2.796
258.76	149.03	2.790
257.76	150.54	2.778
256.81	153.23	2.765
255.25	155.07	2.762
254.19	157.20	2.742
249.55	162.70	2.700
248.26	163.69	2.691
248.23	164.96	2.685

Table 2.

Variation of the overlap matrix spectral radius  $\|S_{ij}\|$  along some points of solution O (see fig. 6).

Conf.	$\ \nabla E\ $	$\ S_{ij}\ $
A	401.7764	2.886
B	999.6724	2.985
C	1000.8692	2.985
D	1002.3634	2.985
E	2219.4795	3.048
F	1776.9051	3.003
G	772.1601	2.875
H	722.8660	2.876
I	723.8417	2.877
J	330.9951	2.739
K	104.8664	2.420
L	90.5965	2.412
II	90.3208	2.412
M	90.3802	2.412
N	112.3853	2.426
O	302.2469	2.685
P	726.1285	2.877
Q	725.3437	2.876
R	724.7618	2.875
S	1822.3083	3.006
T	2213.1819	3.051
U	995.0994	2.984
V	993.5896	2.984
W	992.2199	2.984
X	396.9940	2.882

Table 3.

Gradient norm  $\|\nabla E\|$  and spectral radius  $\|S_{ij}\|$  (see text) for the dynamical system solutions of figure 6 in the final points.

## REFERENCES

- [1] B.F. Schutz, *Geometrical Methods of Mathematical Physics* ( Cambridge University Press, 1980) chap. 2.
- [2] P.G. Mezey, *Theor. Chim. Acta* 58 (1981) 309  
P.G. Mezey, *Theor. Chim. Acta* 63 (1983) 9.
- [3] I.N. Levine, *Quantum Chemistry* ( Prentice-Hall, Englewood Cliffs, NJ, 1991) chap. 16.
- [4] M.W. Hirsch and S. Smale, *Differential Equations, Dynamical Systems and Linear Algebra* (Academic Press, N.York, 1980) chap. 9.
- [5] P. Pechukas, *J. Chem. Phys.* 64 (1976) 1516.
- [6] R.M. Minyaev and D.J. Wales, *Chem. Phys. Lett.* 218 (1994) 413.
- [7] A. Tachibana and K. Fukui, *Theor. Chim. Acta* 49 (1978) 321.  
A. Tachibana and K. Fukui, *Theor. Chim. Acta* 51 (1979) 275.  
K. Fukui, *Acc. Chem. Res.* 14 (1981) 363.
- [8] P.G. Mezey, *J. Am. Chem. Soc.* 112 (1990) 3791.
- [9] M.S. de Giambiagi, M. Giambiagi and F.E. Jorge, *Z. Naturforsch.* 39a (1984) 1259.  
M.S. de Giambiagi, M. Giambiagi and F.E. Jorge, *Theor. Chim. Acta* 68 (1985) 337.  
M.S. de Giambiagi, M. Giambiagi and P. Pitanga, *Chem. Phys. Lett.* 129 (1986) 367.
- [10] H.L. Sellers and L Schäfer, *J. Am. Chem. Soc.* 100 (1978) 7728.
- [11] R.D. Brown, P.D. Godfrey, J.W.V. Storey and M.P. Bassez, *J. Chem. Soc., Chem. Commun.* (1978) 547.
- [12] B.T. Luke, A.G. Gupta, G.H. Loew, J.G. Lawless and D.H. White, *Int. J. Quantum Chem.* 11 (1984) 117.
- [13] K. Iijima, K. Tanaka and S. Onuma, *J. Mol. Struct.* 246 (1991) 257.

- [14] M. Ramek, V.K.W. Cheng, R.F. Frey, S.Q. Newton and L. Schäfer, *J. Mol. Struct.* 235 (1991) 1.
- [15] A.G. Császár, *J. Am. Chem. Soc.* 114 (1992) 9568.
- [16] C.-H. Hu, M. Sen and H.F. Schaefer III, *J. Am. Chem. Soc.* 115 (1993) 2923.
- [17] THOR, Force Field and Molecular Dynamics Simulation, is a software package developed by K.C. Mundim, P.G. Pascutti and P.M. Bisch, to be published.  
E.P.G. Areas, P.G. Pascutti, S. Schreier, K.C. Mundim and P.M. Bisch, *Brazilian J. Med. Biol. Res.* 27 (1994) 527.
- [18] J. Koca and P.H.J. Carlsen, *J. Mol. Struct.* 246 (1991) 165.
- [19] P. Palla, C. Petrongolo and J. Tomasi, *J. Phys. Chem.* 84 (1980) 435.
- [20] B.H. Chirgwin and C.A. Coulson, *Proc. Roy. Soc. London* A201 (1950) 196.
- [21] J.H. Wilkinson, *The Algebraic Eigenvalue Problem* (Clarendon Press, Oxford, 1965) pp. 58-59.
- [22] J.A. Pople and D.L. Beveridge, *Approximate Molecular Orbital Theory* (N.York, McGraw-Hill, 1970).
- [23] J.J.P. Stewart, *J. Comp.-Aided Mol. Design* 4 (1990) 1 (special issue).