

Invariance Criteria and Symmetry Conservation Rules for Geometry Optimizations

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The objective of this paper is to analyze the behaviour of some minimization methods such as steepest descent method, generalized Newton and quasi-Newton methods under transformations of the variables of the function to be minimized. Energy and molecular coordinates are the function and the variables, respectively, in the case of geometry optimizations. Invariant levels are shown to be decisive for the area where the minimization methods can be successfully employed without rescaling of the coordinates. Specific conditions for symmetry conservation are worked out in context of invariant levels. Symmetry making, breaking and conservation are shown with working examples of geometry optimizations and calculation of energy minimum paths on the basis of certain kinds of molecular coordinates.

Key words: Geometry optimization – Symmetry conservation – Transformation of molecular coordinates

1. Introduction

Geometry optimization has become more and more an integral part of quantum-chemical calculations [1–4] and incident thereto a matter of routine. Despite a small number of direct calculations of structures the desire to know the properties of molecules with the atoms in their “theoretical” equilibrium positions is important. Equilibrium geometries correspond to minima in potential energy (\sim hypersurface). In order to localize them, methods of nonlinear programming, especially methods of unconstrained minimization have to be linked with quantum-mechanical approaches. The practicability of programming methods depends mainly on specific characteristics of energy expression. For example, methods which require the knowledge of first partials of the LCAO MO SCF energy [5, 6], or additionally of

second partials [7], enable the user to optimize geometries with highest effectiveness. However, the calculation of these derivatives involves some peculiarities:

1. The demand to have the wave functions as self-consistent as possible [8].
2. The inclusion of *d*-orbitals requires the setting up of analytical formulas much more complicated than for *s*- and *p*-orbitals (the problem is often unsolved [3]—an exception is programme [9]).

Other more general aspects have also to be considered:

3. The proper selection of coordinates of molecular geometry [8] (each of the coordinates has to be rescaled with respect to the other [2]).
4. The problem of conservation of molecular symmetry elements.

The primary aim in writing this paper is twofold: at first the invariance of the minimization methods will be analyzed. The higher the level of invariance against certain transformations of the coordinates the less important is point 3. The second subject will be point 4. Symmetry conservation and symmetry breaking depend essentially on the special coordinates selected and on the specific invariant levels of the method of minimization used, whereas symmetry making is natural for situations in which a higher symmetry than the initial one is energetically favoured.

Pechukas [10] investigated the conservation of symmetry along the steepest descent path on potential hypersurfaces. McIver and Komornicki [5] mentioned that symmetry conservation occurred in the progress of their geometry optimizations and they discussed the relations to the Cartesian coordinates of atoms. However, generalizations have to be made carefully. For example, the assumption of *a priori* validity of symmetry conservation [11] is not justified for all kinds of internal coordinates. As another example, we [12] supposed some artifacts in a geometry optimization [13] of biphenyl. The trouble seems to be due to the special coordinates by means of which initial molecular symmetries (D_2 , D_{2h} , D_{2d}) are not conserved [12].

2. Notations

Internal coordinates such as bondlengths and angles between atoms, useful for describing a fixed molecular structure, are disadvantageous for geometrical changes in the course of unconstrained minimizations. Therefore we shall be concerned only with sets of independent coordinates. In other words, it is assumed that no (equality \sim) constraints exist among the coordinates. As a consequence for practical applications of internal coordinates, curvilinear internal group coordinates may be employed instead of simple internal coordinates [8]. (Note that the use of curvilinear coordinates is not unusual. For example, a formulation of vibrational problems on this basis [14] offers the possibility implicitly to include in the approach anharmonic terms in a very convenient way.) Independent “external” coordinates of atoms are easy to set up, for example by means of the most familiar ones—the Cartesians.

Let an arbitrary set of generally independent coordinates $\{x_i\}_{i=1}^n$ be written in a column vector

$$\mathbf{x} = (x_1, x_2, \dots, x_n)^T. \quad (1)$$

Here superscript T denotes transposition. First partials $g_i = \partial E/\partial x_i$ of the energy E may be represented by the n -vector \mathbf{g} .

$$\mathbf{g} = (g_1, g_2, \dots, g_n)^T. \tag{2}$$

It is well known that a replacement of the $\{x_i\}_{i=1}^n$ by a set of “new” coordinates $\{y_i\}_{i=1}^n$ gives

$$\mathbf{q} = \mathbf{J}^T \mathbf{g}, \tag{3}$$

if $q_i = \partial E/\partial y_i$ and

$$\mathbf{J} = \begin{bmatrix} \partial x_1/\partial y_1 & \dots & \partial x_1/\partial y_n \\ \vdots & & \vdots \\ \partial x_n/\partial y_1 & \dots & \partial x_n/\partial y_n \end{bmatrix} \tag{4}$$

the Jacobian. Let \mathbf{J} be a regular matrix, that is, let $\{x_i\}$ and $\{y_i\}$ be functionally independent. A special relation between $\{x_i\}$ and $\{y_i\}$ consists in the regular linear basis transformation. If \mathbf{y} is the n -vector of the coordinates $\{y_i\}$,

$$\mathbf{x} = \mathbf{T} \mathbf{y}, \tag{5}$$

where \mathbf{T} denotes a regular matrix of constant coefficients.

Relation (3) implies

$$\mathbf{q} = \mathbf{T}^T \mathbf{g}, \tag{6}$$

in other words, \mathbf{T} is identical with the Jacobian

$$\mathbf{T} = \mathbf{J} \tag{7}$$

in this case.

If \mathbf{g} satisfies

$$\mathbf{g} = \mathbf{0}, \tag{8}$$

it is obvious that also

$$\mathbf{J}^T \mathbf{g} = \mathbf{q} = \mathbf{0} \tag{9}$$

for arbitrary \mathbf{J} . Thus stationarity of a point on the potential surface does not depend on the special choice of coordinates. Moreover, it can be assumed for the sake of simplicity that each n -vector \mathbf{x} or \mathbf{y} refers to an orthonormalized basis. Such assumption is usual for Cartesian coordinates. But very often conformational maps show the energy as a function of orthogonal axes too, the latter representing for example two dihedral angles. Although the vector \mathbf{g} (or \mathbf{q}) is often called gradient vector, it may be identified with a “physical” gradient only in cases where it refers to the Cartesian coordinates of atoms.

3. Invariant Levels – a Comparison of Minimization Methods

Minimization methods of the following general recurrence ansatz

$$\mathbf{x}_{i+1} = \mathbf{x}_i - \alpha_i \mathbf{H}_i \mathbf{g}_i \tag{10}$$

are considered, where α is a scalar and H a certain substitute to the inverse Hessian G^{-1} . The second partials $[G]_{ij} = \partial^2 E / \partial x_i \partial x_j$ are the entries of the matrix G . Variants of Eq. (10) define the steepest descent method [15], in which one has

$$H = 1 = \text{const.}, \quad (11)$$

the Newton method [15], where α_i and H_i are given by

$$H_i = G_i^{-1} \quad \alpha = 1 = \text{const.}, \quad (12)$$

and intermediately, various quasi-Newton methods, for which the Fletcher-Powell algorithm [16]

$$H_{i+1} = H_i + A_i + B_i \quad (13)$$

$$A_i = \frac{\Delta x (\Delta x)^T}{(\Delta x)^T \Delta g} \quad B_i = -\frac{H_i \Delta g (\Delta g)^T H_i}{(\Delta g)^T H_i \Delta g} \quad (14)$$

$$\Delta x = x_{i+1} - x_i \quad \Delta g = g_{i+1} - g_i \quad (15)$$

may be representative.

By Eq. (10) we get a sequence of vectors

$$x_0, x_1, \dots, x_i, x_{i+1}, \dots \quad (16)$$

Suppose the recurrence scheme is also applied to basic variables $\{y_i\}$, so that

$$y_{i+1} = y_i - \beta_i K_i q_i, \quad (17)$$

here K in analogy to H denotes a substitute to the inverse of Hessian Q , having the entries $[Q]_{ij} = \partial^2 E / \partial y_i \partial y_j$. Thus a sequence of n -vectors

$$y_0, y_1, \dots, y_i, y_{i+1}, \dots \quad (18)$$

may be obtained. Initially, let Eqs. (10) and (17) be applied to identical molecular structures although the vectors x_0, y_0 satisfy

$$x_0 \neq y_0. \quad (19)$$

Conservation of the identity of the molecular structures for all corresponding iterations of the minimization according to Eqs. (10) and (17), respectively, is an interesting feature. In the following, it will be convenient to call a minimization method to be invariant under a certain transformation of the coordinates, if x_{i+1} represents the same molecular structure as y_{i+1} , assuming that it is the case with x_i and y_i .

Having introduced minimization methods, we proceed to their invariant levels and begin by restricting the relations between $\{x_i\}$ and $\{y_i\}$, defining

$$x_i = T y_i \quad \exists T^{-1}. \quad (20)$$

Again T is a matrix of constant coefficients. Inserting this into the recurrence formula (10) and considering the steepest descent method gives

$$x_{i+1} = T y_i - \alpha_i T^{-1} q_i. \quad (21)$$

Since there is no invariance with respect to linear transformations, relation (20) needs to be further specified. We replace T by an orthogonal transformation

$$T = U \quad U^T U = U U^T = \mathbf{1}, \quad (22)$$

i.e.

$$\mathbf{x}_i = U \mathbf{y}_i. \quad (23)$$

Under this condition we obtain by means of Eq. (17)

$$\mathbf{x}_{i+1} = U \mathbf{y}_i - \alpha_i U \mathbf{q}_i = U(\mathbf{y}_i - \alpha_i \mathbf{q}_i) = U \mathbf{y}_{i+1}. \quad (24)$$

Thus the following theorem is established: *The steepest descent method (Eqs. (10), (11)) is invariant under orthogonal linear transformations of the basic variables of the function to be minimized.*

Upon the theorem a remarkable property can be found in context with the use of Cartesian coordinates of atoms as basic variables. The geometry optimization by means of the steepest descent method is absolutely unaffected by the orientation of the molecules in an external coordinate system. In other words, the internal geometry of a molecule as obtained after a certain number of iterations does not depend on the orientation of the external Cartesian system.

Invariance of the Newton method has been studied recently [8]. In order to complete this work the proof may be repeated briefly. Inserting Eq. (20) into (10), taking into account Eqs. (6), (12) and

$$Q = T^T G T \quad (25)$$

gives

$$\mathbf{x}_{i+1} = T \mathbf{y}_i - T Q_i^{-1} T^T T^{-1} \mathbf{q}_i, \quad (26)$$

which we simplify immediately as

$$\mathbf{x}_{i+1} = T(\mathbf{y}_i - Q_i^{-1} \mathbf{q}_i) = T \mathbf{y}_{i+1}. \quad (27)$$

Thus the *Newton method is invariant under regular linear transformations (including orthogonal ones) of the basic variables of the minimized function.*

The perhaps most remarkable consequence for the actual power of the geometry optimization which follows from the theorem reads: There is absolutely no advantage (only additional computational effort) to use such internal coordinates which are related to the Cartesians by a linear transformation instead of Cartesian coordinates themselves. Certainly, eliminating translation and rotation of the molecules is still necessary in order to avoid the singularity of G (or Q). The point is discussed at the end of the next section.

Invariant levels of quasi-Newton methods depend specifically on the first iteration. Usually the methods iterate the first step down the path of steepest descent. Hence we have

$$H_0 = \mathbf{1} \quad (28)$$

and according to Eqs. (14), (15)

$$\mathbf{B}_1 = -\mathbf{T}^T \mathbf{T}^{-1} \left(\frac{\Delta \mathbf{q} (\Delta \mathbf{q})^T}{(\Delta \mathbf{q})^T \mathbf{T}^{-1} \mathbf{T}^T \mathbf{T}^{-1} \Delta \mathbf{q}} \right) \mathbf{T}^{-1} \quad (29)$$

$$\mathbf{A}_i = \frac{\mathbf{T} \Delta \mathbf{y} (\Delta \mathbf{y})^T \mathbf{T}^T}{(\Delta \mathbf{y})^T \mathbf{T}^T \mathbf{T}^T \mathbf{T}^{-1} \Delta \mathbf{q}} = \mathbf{T} \left(\frac{\Delta \mathbf{y} (\Delta \mathbf{y})^T}{(\Delta \mathbf{y})^T \Delta \mathbf{q}} \right) \mathbf{T}^T \quad (30)$$

so that under assumption of identity (22) \mathbf{A}_i and \mathbf{B}_i satisfy

$$\mathbf{A}_i = \mathbf{U} \left(\frac{\Delta \mathbf{y} (\Delta \mathbf{y})^T}{(\Delta \mathbf{y})^T \Delta \mathbf{q}} \right) \mathbf{U}^T \quad \mathbf{B}_i = -\mathbf{U} \left(\frac{\mathbf{K}_i \Delta \mathbf{q} (\Delta \mathbf{q})^T \mathbf{K}_i}{(\Delta \mathbf{q})^T \mathbf{K}_i \Delta \mathbf{q}} \right) \mathbf{U}^T \quad (31)$$

$$\mathbf{H}_i = \mathbf{U} \mathbf{K}_i \mathbf{U}^T \quad \mathbf{H}_{i+1} = \mathbf{U} \mathbf{K}_{i+1} \mathbf{U}^T. \quad (32)$$

\mathbf{K}_{i+1} is defined according to decomposition (13), replacing $\Delta \mathbf{g}$ by $\Delta \mathbf{q}$, and $\Delta \mathbf{x}$ by $\Delta \mathbf{y}$, respectively. Thus *quasi-Newton methods are at least invariant under orthogonal transformations, that is, invariance at the level of the steepest descent method.*

Now let us assume that \mathbf{H}_0 may have the same transformation properties as \mathbf{G}_0^{-1} . Suppose for example

$$\mathbf{H}_0 = \mathbf{G}_0^{-1}. \quad (33)$$

(Presuming that \mathbf{G}_0 is positively definite, else convergence of the method is questionable.) Thus \mathbf{B}_i fulfills

$$\mathbf{B}_i = -\mathbf{T} \left(\frac{\mathbf{K}_i \Delta \mathbf{q} (\Delta \mathbf{q})^T \mathbf{K}_i}{(\Delta \mathbf{q})^T \mathbf{K}_i \Delta \mathbf{q}} \right) \mathbf{T}^T \quad (34)$$

and interestingly, taking into account relation (30), we can conclude that for the quasi-Newton method the same invariant level applies as for the Newton method itself ($\mathbf{H}_i = \mathbf{T} \mathbf{K}_i \mathbf{T}^T$; $\mathbf{H}_{i+1} = \mathbf{T} \mathbf{K}_{i+1} \mathbf{T}^T$).

Emphasis should be laid on the above-shown invariant levels, particularly attractive properties insofar as they characterize a certain optimality of the different minimization schemes. Newton's method itself is hardly often practicable (exceptions are [7, 11, 17]). If, however, instead of putting \mathbf{H}_0 according to Eq. (28), the inverse Hessian is calculated only initially and subsequently used as a substitute for \mathbf{H}_0 in a quasi-Newton method, then improved convergence will be obtained. This was demonstrated for geometry optimizations by Bloemer and Bruner [7]. The success can be rationalized by taking into consideration the above-shown invariance. In case of unconventional choice of \mathbf{H}_0 according to Eq. (33) the quasi-Newton method fulfills the same optimality criterion as the Newton method itself. Particular dilations and rotations of molecular coordinates do not influence the speed with which the quasi-Newton method converges. Normalization or so-called rescaling of the gradient components as proposed in [2] is consequently superfluous.

4. Discussion of Molecular Symmetry

A molecule is moved under symmetry operations so that its final relative position is indistinguishable from the initial one. If respective symmetry elements are absent

in the molecule both positions can be distinguished and the symmetry operations are normal rotations, reflections, etc. Present molecular symmetry elements may have an effect on the vector \mathbf{x} of coordinates and corrections $\Delta\mathbf{x}$, depending specifically on the type of coordinates used. Criteria upon which symmetry conservation is obtained with minimizations via Eq. (10) will now be shown. For this purpose it is convenient to distinguish between three kinds of coordinates:

1. symmetry-adapted internal coordinates, including curvilinear internal group coordinates,
2. ("external") Cartesian coordinates (note that symmetry conservation rules are given in [5] for the use of such coordinates in quasi-Newton methods) and spherical polar coordinates,
3. coordinates obtained from 1 or 2 by a regular linear transformation.

The three kinds of coordinates will be discussed separately.

4.1. Symmetry-Adapted (Curvilinear) Internal (Group) Coordinates

Molecular symmetry can be expressed in

$$\mathbf{g} = \mathbf{P}^T \mathbf{g} \quad (35)$$

$$\mathbf{G} = \mathbf{P}^T \mathbf{G} \mathbf{P} \quad (36)$$

so that

$$\mathbf{H} = \mathbf{P} \mathbf{H} \mathbf{P}^T \quad (37)$$

and therewith

$$\Delta\mathbf{x} = \mathbf{P} \Delta\mathbf{x}. \quad (38)$$

Here \mathbf{P} is a simple orthogonal matrix, causing permutations of the elements g_i and g_j , if applied on vector \mathbf{g} .

$$\mathbf{P}^T \mathbf{g} = \begin{bmatrix} 1 & & & & & & & & & & & \\ & \ddots & & & & & & & & & & \\ & & 1 & & & & & & & & & \\ & & & 0 & \cdots & 0 & \cdots & 1 & & & & \\ & & & \vdots & 1 & & \ddots & & & & & \\ & & & & & & & & \ddots & & & \\ & & & & & & & & & 1 & & \\ & & & & & & & & & & 0 & \\ & & & & & & & & & & & 1 \\ & & & & & & & & & & & \ddots \\ & & & & & & & & & & & & 1 \end{bmatrix} \begin{bmatrix} g_1 \\ \vdots \\ g_i \\ \vdots \\ g_j \\ \vdots \\ g_n \end{bmatrix} = \begin{bmatrix} g_1 \\ \vdots \\ g_i \\ \vdots \\ g_j \\ \vdots \\ g_n \end{bmatrix} \quad (39)$$

After subtracting an appropriate difference vector \mathbf{a} (normally a zero vector) from \mathbf{x}_i we obtain

$$\mathbf{x}_i - \mathbf{a} = \mathbf{P}(\mathbf{x}_i - \mathbf{a}). \quad (40)$$

whereby

$$\mathbf{g}_i(\mathbf{a}) = \text{const.} \quad \mathbf{H}_i(\mathbf{a}) = \text{const.} \quad (41)$$

Thus subtracting \mathbf{a} on both sides of Eq. (10)

$$\mathbf{x}_i - \mathbf{a} = \mathbf{x}_i - \mathbf{a} - \alpha_i \mathbf{H}_i \mathbf{g}_i \quad (42)$$

one obtains

$$\mathbf{x}_{i+1} - \mathbf{a} = \mathbf{P}(\mathbf{x}_i - \mathbf{a}) - \alpha_i \mathbf{P} \mathbf{H}_i \mathbf{P}^T \mathbf{P} \mathbf{g}_i = \mathbf{P}[\mathbf{x}_i - \mathbf{a} - \alpha_i \mathbf{H}_i \mathbf{g}_i] = \mathbf{P}(\mathbf{x}_{i+1} - \mathbf{a}), \quad (43)$$

which proves the conservation of symmetry for properly chosen (curvilinear) internal (group) coordinates. In other words, molecules described by this kind of coordinates are kept in the initial symmetry by applying minimization methods described by Eq. (10).

4.2. ("External") Cartesian Coordinates, Spherical Polar Coordinates

Let the atomic positions be given by external Cartesian coordinates, then there are only some special cases where the effect of a symmetry operation can be described by a simple permutation matrix \mathbf{P} . Else it is a more general orthogonal matrix \mathbf{R} for rotations and reflections, which has to be applied to \mathbf{g} , \mathbf{H} , \mathbf{x} . We have

$$\mathbf{g} = \mathbf{R}^T \mathbf{g} \quad (44)$$

$$\mathbf{G} = \mathbf{R}^T \mathbf{G} \mathbf{R}. \quad (45)$$

The same holds for external spherical polar coordinates (R, θ, φ) if the centre of molecular symmetry has the coordinates $(R = 0, \theta, \varphi)$. Translations of the centre of the Cartesian coordinates system leave \mathbf{g} and \mathbf{G} constant, and therefore $\Delta \mathbf{x}$. Thus centre of molecular symmetry and centre of the Cartesian coordinates need not be identical for the fulfillment of Eqs. (44), (45). Let the difference vector \mathbf{a} be given, then $(\mathbf{x}_i - \mathbf{a})$ is the vector of atomic coordinates for a Cartesian system, the centre of which is identical with the centre of symmetry so that

$$\mathbf{x}_i - \mathbf{a} = \mathbf{R}(\mathbf{x}_i - \mathbf{a}). \quad (46)$$

Substituting \mathbf{P} by \mathbf{R} in Eq. (43) the conservation of molecular symmetry may be easily shown in the same way as there.

4.3. Coordinates Obtained from Sects. 4.1 or 4.2 by a Regular Non-Orthogonal Linear Transformation

Let the vector \mathbf{x} of the numerical values of the coordinates be obtained by a regular non-orthogonal linear transformation according to Eq. (5). Here \mathbf{y} may be identified

with coordinates introduced under Sects. 4.1 or 4.2 to be suited for symmetry conservation. Hence

$$\mathbf{y} = \mathbf{R}\mathbf{y} \quad (47)$$

$$\mathbf{q} = \mathbf{R}^T\mathbf{q}, \quad (48)$$

but

$$\mathbf{x} = \mathbf{TRT}^{-1}\mathbf{x} \quad (49)$$

$$\mathbf{g} = (\mathbf{TRT}^{-1})^T\mathbf{g}, \quad (50)$$

it is shown that symmetry operations have now to be described by nonorthogonal matrices (\mathbf{TPT}^{-1}). Bearing in mind the invariance levels of the minimization methods it is obvious that neither the steepest descent method nor a conventionally started quasi-Newton method (Eq. (28)) guarantees a conservation of symmetry – more precisely, the first iteration of a geometry optimization on the basis of such coordinates must break the symmetry. However, the Newton- and unconventionally started quasi-Newton methods (Eq. (33)) are invariant with respect to regular linear transformations. Under the assumption initially made that coordinate vector \mathbf{x} is obtained from other coordinates suited for symmetry conservation it is clear that the latter two methods conserve molecular symmetry elements if applied to \mathbf{x} .

There remains the special problem of singularity of \mathbf{G} in cases where $3N$ (N : number of atoms) external coordinates are employed. Strictly speaking, Newton's method need not be discussed if \mathbf{G}^{-1} does not exist. But it was shown in [8] that singularity can be avoided very easily if the origin of the Cartesian system is identical with one atomic position (atom a) and if another atom (b) lies on an axis (say x) whereas the position of a third atom (c) is in a plane spanned by two axes (for example x, y). With this special relative position of the molecule with respect to the coordinate system, the coordinates $x_a, y_a, z_a, y_b, z_b, z_c$ (subscript denotes the atom) can be excluded from the set of minimization variables so that the reduced matrix \mathbf{G}_{red} remains regular. Moreover, it was shown in [8] how to set up a non-orthogonal transformation by which six gradient components vanish so that the respective coordinates remain constant under optimizations. Similar manipulations should be possible with polar spheroidal coordinates, for example. Two conclusions can be made: Symmetry conservation is total with Newton's method in this case of linear transformation of the coordinates 4.1 or 4.2, but steepest descent and quasi-Newton method retain the symmetry of the reduced gradient vector ($3N - 6$ components) only, and therefore the respective symmetry of the $3N - 6$ coordinates of the molecule. (Clearly, convergence rates are also different.)

Another special problem which should be mentioned is that two kinds of symmetry represented by linearity or planarity of the molecules are conserved by geometry optimizations with a broad scale of internal curvilinear coordinates (distances, angles, including dihedral angles between atoms). Changes of atomic distances along the lines through the nuclei cannot change linearity or planarity, whereas changes of the angles between the atoms do not influence planarity. Only changes

of a dihedral angle are capable of distorting planarity. Assuming that each of the respective rotational axes runs through two nuclei one has a symmetrical potential

$$E(\Delta\varphi) = E(-\Delta\varphi) \quad (51)$$

with respect to the dihedral angle φ because the Hamiltonian of free molecules depends on atomic distances only. Thus

$$(\partial E/\partial\varphi)_{\Delta\varphi=0} = 0. \quad (52)$$

As a consequence, the use of internal coordinates defined by means of the atoms only guarantees the conservation of planarity and linearity of the molecules along the path of optimization of their geometry.

5. Numerical Examples

Geometries of some molecules were optimized to give examples of symmetry conservation, symmetry breaking and making along the path of minimization. When making the choice of coordinates and molecules, emphasis has been laid on the ease of insight into the run of minimization. OCS and the anion $(\text{Cl}_2\text{I})^-$ satisfy the criterion. The molecules provide numerically simple but instructive illustrations of the basic principles derived in the previous sections. The CNDO/2 energy [18] was the function to be minimized. *d*-orbitals for sulphur, chlorine and iodine were included. Parameters for the iodine atom have been chosen according to [19]. The CNDO/2 was implemented by the author of this paper [9] in the quasi-Newton subroutine VA09A, which has become popular in solving geometry optimization problems [9, 12, 20, 21]. Main features of the programme [9] are that first partial derivatives with respect to curvilinear coordinates of the molecular geometry can be calculated explicitly by using analytical expressions as well as its scope from hydrogen to iodine. Methodical aspects were described particularly in [8, 12, 20].

5.1. $(\text{Cl}_2\text{I})^-$

Two sets of coordinates 1 and 2 of the molecular geometry were formed:

1. *bondlengths* $R(\text{I}, \text{Cl}^1) = y_1$
 $R(\text{I}, \text{Cl}^2) = y_2$
2. *distances* $R(\text{I}, (\text{Cl}^1, \text{Cl}^2)) = x_1$
 $R(\text{Cl}^1, \text{Cl}^2) = x_2.$

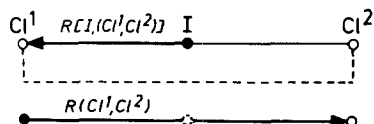
The chlorine atoms are marked by superscripts for distinction. x_1 is the distance from the iodine atom to the group $(\text{Cl}^1, \text{Cl}^2)$ and x_2 is the distance of the non-bonded chlorine atoms. Figure 1 shows the geometrical model to start with.

$$y_1 = y_2 \quad (53)$$

implies

$$\partial E/\partial y_1 = \partial E/\partial y_2. \quad (54)$$

Fig. 1. $(\text{Cl}_2\text{I})^-$: arrows denote geometry parameters – filled circles: atoms unaffected under variations of the geometry parameters



This leads to the consequence that the parameter set 1 is suitable for conserving the initial symmetry $D_{\infty h}$ along the path of geometry optimization since the whole model has been constrained to collinearity. It should be mentioned that only one degree of freedom appears effective, although two parameters (y_1 and y_2) may be used explicitly. Under these circumstances the advanced minimization method [22] is reduced to the classical regula falsi.

The parameter set 2 is suitable for conserving the symmetry $C_{\infty v}$ only. This can be easily seen with Fig. 1. The gradient vector reads initially

$$\begin{bmatrix} 1 & -1 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} \partial E / \partial y_1 \\ \partial E / \partial y_2 \end{bmatrix} = \begin{bmatrix} \partial E / \partial x_1 \\ \partial E / \partial x_2 \end{bmatrix} = \begin{bmatrix} 0 \\ \partial E / \partial y_2 \end{bmatrix}. \quad (55)$$

Thus, let $\partial E / \partial x_2 \neq 0$ then it is immediately obtained that the minimization of $E(x_1, x_2)$ yields $y_1 \neq y_2$ after a single iteration so that the symmetry $D_{\infty h}$ is broken or, more precisely, reduced to $C_{\infty v}$. However, $D_{\infty h}$ was restored with high accuracy after achieving convergence. The minimization histories 1 and 2 are listed in Table 1. Explicitly optimized coordinates x_1, x_2 are converted into the more familiar y_1, y_2 for comparisons. The minimization was not sensitive to the non-orthogonal linear transformation relating 1 to 2. An almost identical number of iterations indicates that the estimation of the force constant matrix was successful in the course of the minimization of $E(x_1, x_2)$ and $E(y_1, y_2)$ as well.

Table 1. Geometry optimization history of the Cl_2I^- molecule. (Relative energy: $E_{\text{rel}} = E + 45.592243290$ a.u.; bondlengths in Ångstrom units)

Iteration	$D_{\infty h}$ conserved		$R_{\text{I-Cl}^1}$ [Å]	$R_{\text{I-Cl}^2}$ [Å]	$C_{\infty v}$ conserved	
	E_{rel} [a.u.]	$R_{\text{I-Cl}}$ [Å]			$R_{\text{I-Cl}^2}$ [Å]	E_{rel} [a.u.]
0	0.030861027	2.1	2.1	2.1	0.030861027	
1	0.004352203	2.02850	2.1	2.02850	0.017430183	
2	0.000414418	1.97715	2.03099	1.97539	0.002620658	
3	0.000003365	1.98998	1.97609	1.99023	0.000242475	
4	0.000000002	1.98894	1.99025	1.98915	0.000002683	
5	0.0	1.98891	1.98895	1.98889	0.000000002	
6	<i>convergent</i>		1.98891	1.98892	0.0	

5.2. OCS

Two parameter sets of the molecular geometry were defined:

3. bondlengths $R(\text{C}, \text{O}) = y_1$
 $R(\text{C}, \text{S}) = y_2$

4. *bondlength* $R(C, O) = x_1$
distance $R(Hp, S) = x_2$
angle $\sphericalangle C, Hp, S = x_3$.

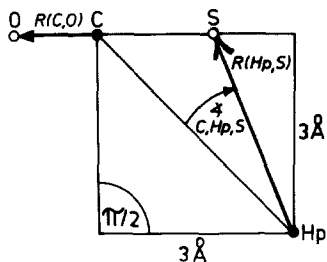


Fig. 2. OCS: arrows denote geometry parameters 4—the carbon atom and the helpoint Hp are fixed

The initial model and the parameter set 4 are shown in Fig. 2. There exists no linear relation between 3 and 4. The coordinates 3 are sufficient to retain the initial symmetry $C_{\infty v}$. In the case of set 4 the collinearity of the atoms is disturbed within the first iteration of the minimization. The complete progress of minimizing $E(y_1, y_2)$ and $E(x_1, x_2, x_3)$ is listed in Table 2, where x_2, x_3 are converted into $R(C, S)$ and $\sphericalangle O, C, S$. It can be seen that the equilibrium geometry and therefore $C_{\infty v}$ symmetry was accurately achieved on the basis of coordinates 4 after 14 iterations. This number is large compared with the minimization of $E(y_1, y_2)$, which is considerably more efficient because only 6 iterations were required to reach the minimum. The discrepancy is caused by the improper choice of coordinates 4 which are not only in contrast to the chemical bond conception. In addition, no linear transformation exists that improves the situation.

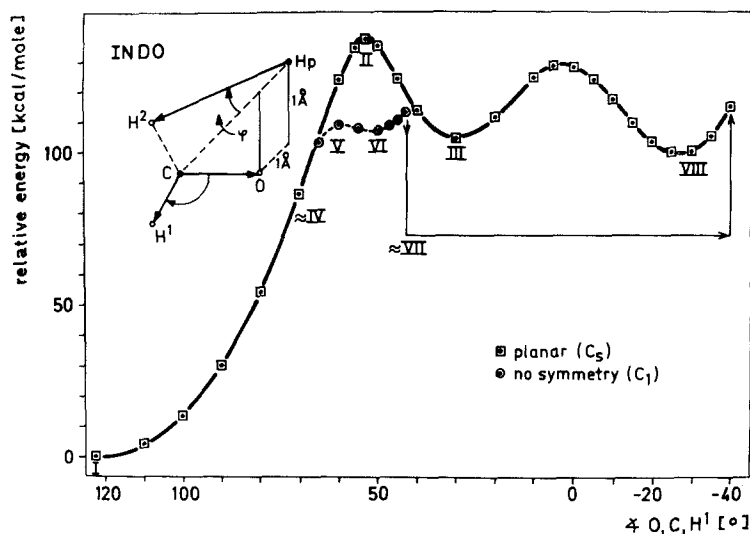
5.3. H_2CO

Since the relevant stationary states are those with higher symmetry ($(Cl_2I)^- : D_{\infty h}$; OCS; $C_{\infty v}$) the respective stationary points were also reached along the path of minimization of $E(x_1, x_2)$ and $E(x_1, x_2, x_3)$. Clearly, coordinates like $R(I, (Cl^1, Cl^2))$, $R(Hp, S)$, $\sphericalangle C, Hp, S$ are artificial and their choice was made only for illustration. But there may be problems which could be solved quite easily by setting up such unconventional parameters of the molecular geometry.

A possible example is the energy minimum path for the formaldehyde-hydroxycarbene rearrangement. Normally, the symmetry C_s is conserved along this path and this is the reason why there is no simple saddle point along this path, as pointed out recently [23]. However, a set of coordinates which does not cause conservation of planarity (Fig. 3) gives the simple saddle points *V*, *VII* and minimum *VI* (numbering according to [23]) and thus a quite similar result as the special procedure developed by Panciř [24]. The calculated energy minimum paths are shown in Fig. 3. (Note that the INDO method has been employed here in order to enable comparisons with [23].) Panciř's approach requires the matrix G of second partials in order to calculate reaction paths without symmetry constraints. This implies expensive computational effort, but the optimization with properly chosen coordinates by means of which the symmetry can be broken has the advantage of economy.

Table 2. Geometry optimization history of the OCS molecule. (Relative energy: $E_{\text{rel}} = E + 36.119916607$ a.u.; bondlengths in Ångstrom units, bond angle in degrees $- 360^\circ = 2\pi$)

Iteration	$C_{\infty v}$ conserved				C_s conserved		
	E_{rel} [a.u.]	$R_{\text{C-O}}$ [Å]	$R_{\text{C-S}}$ [Å]	$R_{\text{C-S}}$ [Å]	$R_{\text{C-O}}$ [Å]	$\angle \text{O, C, S}$ [°]	E_{rel} [a.u.]
0				1.75	1.3	180.0	0.040593802
1				1.14189	1.24175	161.297	no SCF-convergence
0	0.040593802	1.3	1.75	1.71369	1.20344	180.0	0.002975516
1a	0.034479050	1.12731	1.68505	0.99744	1.21567	147.448	1.647971589
1b	0.002974887	1.20344	1.71369	1.69698	1.20366	179.763	0.001487639
2	0.000486590	1.20990	1.68331	1.66683	1.21898	179.338	0.000198332
3	0.000014289	1.21241	1.65994	1.65954	1.21109	179.242	0.000041295
4	0.000000150	1.21291	1.66333	1.66342	1.21274	179.303	0.000007453
5	0.000000001	1.21275	1.66315	1.66327	1.21277	179.310	0.000007247
6	0.0	1.21277	1.66314	1.66312	1.21279	179.327	0.000006367
7		<i>convergent</i>		1.66294	1.21281	179.365	0.000006165
8				1.66273	1.21284	179.443	0.000004906
9				1.66251	1.21287	179.606	0.000002846
10				1.66245	1.21288	179.929	0.000000667
11				1.66269	1.21284	179.998	0.000000255
12				1.66305	1.21278	179.976	0.000000097
13				1.66316	1.21275	179.993	0.000000002
14				1.66314	1.21277	179.999	0.0


Fig. 3. INDO-Energy minimum paths for the formaldehyde-hydroxycarbene rearrangement (*I*: formaldehyde, *III*: trans-hydroxycarbene, *VIII*: cis-hydroxycarbene); inset: geometry parameters suited for breaking the symmetry C_s

References

1. Slanina, Z., Schlanger, J., Zahradnik, R.: *Coll. Czechoslov. Chem. Commun.* **41**, 1864 (1976)
2. Collins, J. B., Schleyer, P. v. R., Binkley, J. S., Pople, J. A.: *J. Chem. Phys.* **64**, 5142 (1976)
3. Dewar, M. J. S., Ford, G. P.: *J. Am. Chem. Soc.* **99**, 1685 (1977)
4. Catalán, J., Macias, A.: *J. Mol. Struct.* **38**, 209 (1977)
5. McIver Jr., J. W., Komornicki, A.: *Chem. Phys. Letters* **10**, 303 (1971)
6. Panciř, J.: *Theoret. Chim. Acta (Berl.)* **29**, 21 (1973)
7. Bloemer, W. L., Bruner, B. L.: *J. Chem. Phys.* **58**, 3735 (1973)
8. Scharfenberg, P., Sklenar, H. in: *Quantitative structure-activity analysis (Suhl 1976)* p. 175. Berlin: Akademie-Verlag 1978
9. Scharfenberg, P.: *BIENE2—Ein Programm zur Bestimmung der Gleichgewichtsgeometrie großer Molekeln.* Berlin 1975
10. Pechukas, P.: *J. Chem. Phys.* **64**, 1516 (1976)
11. Török, F., Hegedüs, A., Pulay, P.: *Theoret. Chim. Acta (Berl.)* **32**, 145 (1973)
12. Scharfenberg, P., Jung, C.: *Chem. Phys. Letters* **57**, 131 (1978)
13. Rayez, J. C., Dannenberg, J. J.: *Chem. Phys. Letters* **41**, 492 (1976)
14. Quade, C. R.: *J. Chem. Phys.* **64**, 2783 (1976); **69**, 1321 (1978)
15. Hoffmann, U., Hofmann, H.: *Einführung in die Optimierung.* Weinheim: Verlag Chemie 1971
16. Fletcher, R., Powell, M. J. D.: *Comput. J.* **6**, 163 (1963)
17. Warshel, A., Karplus, M.: *J. Am. Chem. Soc.* **94**, 5612 (1972)
18. Pople, J. A., Beveridge, D. L.: *Approximate molecular orbital theory.* New York: McGraw-Hill 1970
19. Galasso, V.: *Theoret. Chim. Acta (Berl.)* **34**, 137 (1974)
20. Scharfenberg, P.: *Theoret. Chim. Acta (Berl.)* **49**, 115 (1978)
21. Scharfenberg, P.: *Z. Chem.* **17**, 388 (1977)
22. Fletcher, R.: *FORTRAN subroutines for minimization by quasi-Newton methods—VA09A.* Harwell 1972
23. Panciř, J.: *Coll. Czechoslov. Chem. Commun.* **42**, 16 (1977)
24. Panciř, J.: *Coll. Czechoslov. Chem. Commun.* **40**, 1112 (1975)

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