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Analysis of Critical Points on the Potential Energy Surface

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A simple classification scheme is proposed for critical points, based only on rank r and signature s of the (n, n)-matrix $\boldsymbol{G}$ of harmonic force constants. The determination of r and s, e.g. by the well-known factorization $\boldsymbol{G} = \boldsymbol{L}^T\boldsymbol{g}\boldsymbol{L}$ ($\boldsymbol{L}$: triangular matrix, $\boldsymbol{g}$: diagonal matrix), has several theoretical as well as practical (computational) advantages over the inspection of eigenvalues of $\boldsymbol{G}$, so far used in quantum chemistry. The eigenvalues are sufficient but *not* necessary for a classification whereas rank and signature are the only necessary and sufficient prerequisites for solving the task. For the purpose of presenting a working example, by calculating only a 2×2 torque constant matrix, it is shown that the coplanar ethylbenzene is unstable in the CNDO/2 picture.

Key words: Critical points – Potential energy surface – Analysis of force constant matrix – Classification method for critical (i.e. stationary) points – Ethylbenzene.

1. Introduction

Potential energy surfaces may be calculated by means of one of several quantum chemical approaches, based on Hartree–Fock and/or configuration interaction methods or estimated semiempirically. It is well known that emphasis is often laid on the localization of critical points, i.e. points where energy as a function of coordinates becomes stationary. To solve the task of finding such points, the so-called geometry optimization methods should be used instead of calculating the surface point by point. The best known more advanced techniques are those which minimize the energy down the line of conjugate direction, the line of steepest descent or *quasi*-Newton methods, respectively. To apply the latter, it is

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necessary to know the first partial derivatives $\partial E/\partial \xi$ of the energy E with respect to coordinates $\{\xi_i\}$ of the molecular geometry. Analytical calculations of the derivatives [1, 2] increase efficiency compared with numerical calculations [3]. Minimizing $\sum (\partial E/\partial \xi_i)^2$, some of these geometry optimization methods are also used for calculations of transition states [4], despite the most familiar alternative of computing minimum energy paths or the steepest descent paths. Critical points on such paths are also critical points on the potential surface. It can be found that these points have been studied in literature [5] from several special aspects.

In order to analyze or to classify critical points, respectively, McIver and Komornicki [4] introduced the eigenvalue calculation, i.e. the diagonalization

$$\boldsymbol{U}^T\boldsymbol{G}\boldsymbol{U} = \boldsymbol{d}$$

of the harmonic force constant matrix $\boldsymbol{G}$, the entries of which read

$$[\boldsymbol{G}]_{ij} = \partial^2 E/\partial \xi_i \, \partial \xi_j.$$

$\boldsymbol{U}$ is an orthogonal matrix whereas $\boldsymbol{d}$ has a diagonal form, containing the eigenvalues $\{d_i\}$ of $\boldsymbol{G}$. To classify a critical point, the positive, negative and zero diagonal elements of $\boldsymbol{d}$ have then to be counted separately without consideration of their absolute values. Even here it may be suspected that eigenvalues provide more information than absolutely necessary for solving a classification problem; in other words, their knowledge is sufficient but may be *not* necessary.

The most expansive step consists in the calculation of $\boldsymbol{G}$. In addition, eigenvectors can be computed only iteratively, and therefore eigenvalues too. $\boldsymbol{U}$ can be written as the product of an infinite number of elementary orthogonal matrices, being reduced to an appropriate finite number. Therefore it is not easy to estimate *a posteriori* rounding and cut-off errors as well as their influence on the signs of the $\{d_i\}$. Another drawback of eigenvalue calculations is the occurrence of instabilities with eigenvalues which satisfy

$$|d_i| \ll |d_k|.$$

The possibility of achieving relevant *a priori* estimations of the signs of $\{d_i\}$ depends specifically on the numerical values of the entries of $\boldsymbol{G}$. Only rarely this can be done uniquely by Gerschgorin's theorem.

The geometry optimization provides us with theoretical molecular structures and conformations, structures of molecular complexes such as optimized solvate shells. Next of all it becomes necessary to decide whether these structures are stable or not [6]. To put it more precisely, unstable species which belong to simple or higher order saddle points have to be excluded. They can be recognized on one or more negative eigenvalues $\{d_i\}$. From a practical view point it is desirable to have a simpler approach than the calculation of eigenvalues of the force constant matrix. (On the other hand, it is necessary that $\boldsymbol{G}$ will have to be diagonalized if normal vibrations or related spectroscopic properties are desired.)

It will be shown how the practical task of classification can be solved for a considerable part of problems knowing a marginal part of $\boldsymbol{G}$ and very economically so, especially for larger molecules. Such progress becomes possible on the basis of necessary and sufficient criteria, derived in the next section.

2. Method

Replacement of a given set of curvilinear coordinates $\{\xi_i\}_{i=1}^{n}$ by another functionally independent set $\{\chi_i\}_{i=1}^{n}$ results in a transformation

$$\boldsymbol{Q} = \boldsymbol{J}^T \boldsymbol{G} \boldsymbol{J} + \sum_{i=1}^{n} (\partial E/\partial \xi_i) \boldsymbol{\Delta}(\xi_i)$$

of the matrix of second derivatives, where $\boldsymbol{J}$ is the Jacobian

$$[\boldsymbol{J}]_{ij} = \partial \xi_i / \partial \chi_j$$

and

$$[\boldsymbol{\Delta}(\xi_i)]_{kl} = \partial^2 \xi_i / \partial \chi_k \, \partial \chi_l$$

$$[\boldsymbol{Q}]_{ij} = \partial^2 E / \partial \chi_i \, \partial \chi_j,$$

respectively. The second term on the right side of the above equation will vanish at critical points because all $\partial E/\partial \xi_i$ vanish according to the definition of such points. As a consequence, the nature of critical points can be understood by theory of quadratic functions (or so-called surfaces of second degree), which is associated with quadratic forms, although energy E need not be of that kind. The remaining special relation

$$\boldsymbol{Q} = \boldsymbol{J}^T \boldsymbol{G} \boldsymbol{J}$$

is called a congruent transformation, realizations including mass weighting of the coordinates as well as the diagonalization mentioned in the preceding section. As stated by the well known law of inertia of quadratic forms [7], rank r and signature s of $\boldsymbol{G}$ remain constant under congruent transformations. In other words, if the matrix is brought to an arbitrary diagonal form (the diagonal need not contain the eigenvalues), one counts

$\frac{1}{2}(r+s)$ *positive elements,*

$\frac{1}{2}(r-s)$ *negative elements,*

$(n-r)$ *zero elements.*

Therefore r, s, n of $\boldsymbol{G}$ determine uniquely the natue of a critical point:

maximum $s=-n, \quad r=n$

minimum $s=n, \quad r=n$

simple saddle point $s=n-1 \quad r=n$

higher order saddle point, $s=n-k$ *(order* $k>1$*)* $r=n$.

Thus, in order to classify critical points, the factorization

$$\boldsymbol{G} = \boldsymbol{L}^T \boldsymbol{g} \boldsymbol{L}$$

might be applied instead of eigenvalue calculation. $\boldsymbol{L}$ is a triangular matrix, either a lower or an upper one, and $\boldsymbol{g}$ is a diagonal matrix. If

$$l_{i<j} = 0 \qquad l_{if} = [\boldsymbol{L}^T]_{ij},$$

i.e. $\boldsymbol{L}^T$ lower triangular matrix, and $\boldsymbol{L}$ with unit diagonal

$$l_{ii} = 1 \qquad (i = 1, \ldots, n)$$

then $\{g_i\}$ and $\{l_{ik}\}$ may be calculated consecutively according to

$$l_{ik} = \left([\boldsymbol{G}]_{ik} - \sum_{j=1}^{k-1} l_{ij} l_{kj} g_j \right) g_k$$

$$g_i = [\boldsymbol{G}]_{ii} - \sum_{j=1}^{i-1} l_{ij}^2 g_j.$$

Alternatively, instead of putting l_{ii} equal one, it is also possible to assign the numerals ±1 to g_i so that

$$l_{ii} = \left([\boldsymbol{G}]_{ik} - \sum_{j=1}^{i-1} l_{ij}^2 g_j \right)^{1/2}.$$

3. Discussion

The determination of rank and signature by factorization of $\boldsymbol{G}$ has some advantages over the eigenvalue calculation:

(i) A very simple algorithm, making also calculations on a mini-computer possible
(ii) A numerically almost stable procedure
(iii) No iterative method
(iv) Errors ε in $\boldsymbol{G}$ can easily be analyzed by factorizing $\boldsymbol{G}$ with $g_{ij} + \varepsilon$ and also with $g_{ij} - \varepsilon$
(v) *A priori* estimations of $\boldsymbol{g}$ are possible.

A subject of practical value runs as follows: Let the task be the elimination of unstable species, i.e. finding of saddle points (of simple or higher order), then the method can save an enormous computational effort. The gradient vector

$$\boldsymbol{\partial E / \partial \xi} = (\partial E / \partial \xi_1, \ldots, \partial E / \partial \xi_n)^T$$

may be calculated analytically or numerically. The j-th column or row ($\boldsymbol{G} = \boldsymbol{G}^T$) of $\boldsymbol{G}$ is then obtained either by [8]

$$\frac{\Delta(\boldsymbol{\partial E / \partial \xi})_{\xi_j}}{\Delta \xi_j}$$

or more precise numerical differentiation than the calculation of the quotient of differences. Each of these rows of $\boldsymbol{G}$ can be factorized immediately, and the procedure can be skipped if the first g_i appears which satisfies

$$g_i < 0.$$

Presupposing that the coordinates $\{\xi_i\}$ have been well chosen, only a small block of $\boldsymbol{G}$ [concerning "weak" (conformational) degrees of freedom] is necessary to identify a structure as unstable. This can be shown with a working example: The structure of the coplanar conformation of ethylbenzene, as shown in the figure, was optimized within the CNDO/2 approach. For this purpose a method was applied using analytically calculated first partial derivatives of the energy with respect to curvilinear internal coordinates [1, 2, 9, 10] along with Fletcher's minimization procedure VA09A [11]. The optimized geometry is also shown (Table 1). The second partial derivatives were estimated by calculating $\partial E/\partial\tau$ after addition of small increments $\Delta\tau_i$ to the equilibrium structure. τ_1 is a dihedral angle for rotation of the phenyl moiety and τ_2 describes the rotation of the methyl group. With

$$\Delta\tau_i = 2^0 \hat{=} 4\pi/360 \qquad (i = 1, 2)$$

the force or rather torque constant matrix reads (in a.u. without weighting with reduced moments of inertia)

$$10^{-5}\begin{bmatrix} 9.756 & 829.2 \\ 817.3 & 2819.0 \end{bmatrix} \approx 10^{-5}\begin{bmatrix} 1.0 & 0 \\ 83.9 & 1.0 \end{bmatrix}\begin{bmatrix} 9.76 & 0 \\ 0 & -65851.0 \end{bmatrix}\begin{bmatrix} 1.0 & 83.9 \\ 0 & 1.0 \end{bmatrix}$$

leaving out the remaining elements of the first two rows of $\boldsymbol{G}$. (The complete cartesian force constant matrix of ethylbenzene is a 54 × 54 one, whereas internal coordinates reduce the dimension to 48 × 48.)

The influence of the individual errors present in the numerical values of the force constants can easily be described quantitatively with regard to the results of classification. Deviations of $\boldsymbol{G} - \boldsymbol{G}^T$ from the zero-matrix indicate errors of such kind. In the context of the above example it can be proved that compensation of errors cannot cause changes of the signs of $\{g_i\}$. Thus coplanar ethylbenzene is unstable in the CNDO/2 picture. (Notice that such a result agrees with experiments [12] as discussed in [13].) The same holds for substituted species as phenylethylamine, dopamine or related biogenic amines and their cations, as has

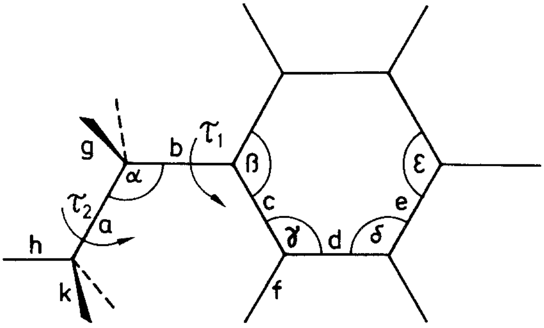

Fig. 1. Coplanar model of ethylbenzene

been shown recently [13]. Other examples, concerning the stability of pentacoordinated compounds, are considered in [14]. There are two possibilities to avoid problems due to present rotational and/or translational degrees of freedom if cartesian or related force constant matrices have to be analyzed.

(i) Permutations of rows and columns of $\boldsymbol{G}$ shift numerical problems, indicated by

$$[\boldsymbol{G}]_{ii} \approx \sum_{j=1}^{i-1} l_{ij}^2 g_j$$

to the end of the factorization process until only $n-k$ rows remain to be factorized, i.e. just the number of rotational and translational degrees of freedom (normally $n-k=6$).

(ii) Under special conditions molecule-fixed cartesian coordinates may also be set up easily by excluding six of the $3N$ (N: number of atoms) coordinates [2, 10]. In addition, a congruent transformation can also be constructed for this purpose, having the same effect as the exclusion of some coordinates [2, 10].

Table 1. Optimized geometry (CNDO/2) of the coplanar ethylbenzene molecule

Internal Coordinates			
a	1.4665	α	117.14
b	1.4687	β	115.63
c^a	1.3961	γ^a	122.64
d^a	1.3834	δ^a	119.97
e^a	1.3841	ε	119.00
f^a	1.1180		
g	1.1273		
h	1.1210		
k	1.1202		
Cartesian Coordinates			
C	−0.05129	0.0	0.0
C	0.70726	−1.17107	0.0
C	2.09145	−1.16262	0.0
C	2.77792	0.03845	0.0
C	2.05963	1.22233	0.0
C	0.67737	1.19190	0.0
H	0.18227	−2.15969	0.0
H	2.65139	−2.12947	0.0
H	3.89484	0.05343	0.0
H	2.59420	2.20340	0.0
H	0.12259	2.16393	0.0
C	−1.52000	0.0	0.0
C	−2.18898	−1.30499	0.0
H	−1.88539	0.59405	0.88570
H	−1.88539	0.59405	−0.88570
H	−3.30544	−1.20447	0.0
H	−1.93227	−1.92138	0.89950
H	−1.93227	−1.92138	−0.89950

[a] Mean value.

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