Efficient and stable method of searching for optimum structures of molecules containing cyclic parts

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An efficient and stable method of searching for optimum structures of molecules containing cyclic parts is proposed, where both the Cartesian and the internal coordinates are improved independently at each iteration of the optimization, and are used for the next geometry of the cyclic parts and of the remaining parts, respectively. The utilization of the Cartesian coordinates at the cyclic parts allows us to avoid the disastrous and irrecoverable distortions, which frequently occur if one uses the internal coordinates. For the remaining parts, the internal coordinates are used, so that an efficient calculation is obtained. The present method is tested in the search for the geometries of pyridine and ethylene oxide in the ground state and compared with the usual methods which employ either the internal coordinates or the Cartesian coordinates as optimization variables; our new method is found to be more efficient and more stable than the usual methods.

1. Introduction

The search for the structures of molecules in the equilibrium and transition states is one of the essential steps in theoretical studies of physical properties and chemical reactions of molecular systems. Since Murtagh and Sargent [1] proposed the optimization method and McIver and Komornicki [2] first applied it to molecular systems, the method has been extensively used. The method has also been improved [3-10], as reviewed by Head and Zerner [11], by appending the linear-search method to bring the geometry far removed from the optimum structure into the range of convergence and by adopting the rank-2 method to update the approximate second derivative of the total energy. Though the method is formulated for general coordinate systems, the internal coordinate system has been overwhelmingly used rather than the Cartesian coordinate system; this is because the former gives faster convergence and is convenient in fixing some parts of a molecule. Thus, the method has been equipped fully for the optimization of non-cyclic molecules. Problems, however, seem to remain for the optimization of cyclic molecules since the use of the internal coordinates results in disastrous and irrecov-

erable distortions of cyclic parts, and the use of the Cartesian coordinates demands a large number of iterations. A better method for the optimization of molecules containing cyclic parts seems to be necessary.

The drastic distortion occurring when one uses the internal coordinates originates in the fact that some internal coordinates are unnecessary to locate atoms in the cyclic parts. The geometry of an N-membered planar ring, for instance, can be specified without the use of one of the bond distances and the two angles at both corners of the bond. These unnecessary internal coordinates of course, do not participate in the optimization variables. These coordinates are determined indirectly through the participating coordinates, so that they may change drastically as a consequence of accumulation of small changes of the participating coordinates. In other words, such important interactions of atoms are not taken into account explicitly although they significantly affect the structure of the cyclic parts. The absence of the strong interactions is fatal in searching for the optimum structures of molecules containing cyclic parts.

In order to circumvent this difficulty, we usually use the Cartesian coordinates as optimization variables. In this case, the *position* of each atom in the

Cartesian coordinate system is optimized depending on the interactions with all the remaining atoms, so that such a critical distortion does not take place. The problems of this method are that (1) it is less efficient than the method with the internal coordinates, and (2) all the atoms should be optimized with these coordinates even if the cyclic part is just a small portion of the whole molecule. It is, therefore, desirable to have a method where the non-cyclic parts are optimized with the help of the internal coordinates in order to keep high efficiency, and the cyclic parts with the Cartesian coordinates to get stability. The purpose of the present work is to propose such an efficient and stable method for the optimization of structures of molecules containing cyclic parts.

2. Method

In usual ab initio calculations, the optimum geometry is searched for by the pseudo-second-order method [11], where the analytical first derivative g_0 of the total energy, evaluated at the current coordinates R_0, and the approximate second derivative H, which will be improved at each cycle of the optimization, are used to get new coordinates R via

$$R = R_0 - H^{-1} g_0 . \tag{1}$$

The internal coordinates are usually used as a coordinate system of R and R_0, and the Cartesian coordinates are rarely employed. In the present method, however, both the internal and the Cartesian coordinates are used and optimized.

First of all, we classify the atoms in the cyclic parts into groups; the first group includes only the atoms constituting the first cyclic part, the second group consists of those in the second cyclic part, and so on. The atoms in the non-cyclic parts belong to neither of the above groups. Then we sort the internal coordinates into two groups; the first group $R^{(1)}$ consists of the internal coordinates defined only by the atoms within the same group of atoms, and the second group $R^{(2)}$ consists of the remaining coordinates, such as those defined by atoms in different groups, or in the non-cyclic parts.

Now, we give the present optimization method. The method consists of the following steps, and they are repeated until the optimum geometry is found:

(1) The present geometry, expressed in terms of the internal coordinate system R_{I0} and the Cartesian coordinate system R_{C0}, is improved independently by the use of eq. (1) as

$$R_I = R_{I0} - H_I^{-1} g_{I0} , \tag{2}$$

$$R_C = R_{C0} - H_C^{-1} g_{C0} . \tag{3}$$

(2) The new geometry R_{IC}, in terms of the internal coordinate system, is generated from the improved ones R_I and R_C; the internal coordinates in the first group $R_{IC}^{(1)}$ are set equal to those transformed from the Cartesian coordinates R_C, and the remaining internal coordinates belonging to the second group $R_{IC}^{(2)}$ are set equal to those in R_I,

$$R_{IC} = \begin{pmatrix} R_{IC}^{(1)} \\ R_{IC}^{(2)} \end{pmatrix}$$

$$= \begin{pmatrix} \text{the first group coordinates of transformed } R_C \\ \text{the second group coordinates of } R_I \end{pmatrix} . \tag{4}$$

(3) The R_{IC}, thus obtained, are used as R_{I0} in the next cycle of the optimization, are transformed into the Cartesian coordinates and stored in R_{C0} for the next calculation by eq. (3).

(4) The first derivatives g_{I0} and g_{C0} are calculated at the new geometry, and the second derivatives H_I and H_C are improved by the usual method [11].

The second step corresponds to optimizing the cyclic parts with the Cartesian coordinates and the remaining parts with the internal coordinates. Thus, the disastrous distortions of the cyclic parts can be avoided, and high efficiency is anticipated for the optimization of non-cyclic parts.

Other characteristic features of the present method are as follows:

(1) The pseudo-second-order method is employed to get R_I and R_C, and then the present method also assumes the quality of the pseudo-second-order convergence in so far as the coupling between the groups $R_{IC}^{(1)}$ and $R_{IC}^{(2)}$ is small.

(2) A linear search, if one wishes, is possible by the use of the R_{IC} as

$$R_{IC}(\alpha) = R_{I0} + \alpha (R_{IC} - R_{I0}) , \tag{5}$$

with α representing the step length to be determined.

This search guarantees that the cyclic parts are not drastically deformed.

(3) The advantages of employing the internal coordinates, so as to be able to fix some parts of molecular structure, are retained since the internal coordinate system is used to express the modified geometry R_{IC}.

(4) The present method unifies the method employing only the internal coordinates and that employing only the Cartesian coordinates, since the present method results in them if we intentionally specify *no* atom to be in a cyclic part or *all* the atoms to be in a cyclic part, respectively.

(5) The present method is applicable to any method for obtaining the new R_I and R_C, since the key of our procedure is to combine the new coordinates R_I and R_C, independently of how they are obtained.

The implementation of the present method can be readily accomplished; the optimization procedures with both the internal and the Cartesian coordinates are usually installed in ab initio program systems, and the evaluation of the internal coordinates from the Cartesian coordinates, carried out at the second step, is a simple task. The grouping of the internal coordinates into $R_{IC}^{(1)}$ and $R_{IC}^{(2)}$ can be easily performed by the use of the grouping of atoms, which is given beforehand. The grouping of atoms is independent of which distances, angles and dihedral angles of bonds are chosen as the optimization variables and how the optimization variables are ordered, so that it is convenient in practical calculations to give the groups of atoms rather than those of the internal coordinates.

It may be noteworthy that the transformation from the Cartesian coordinate system to the internal coordinate system is non-linear. This means that the Taylor expansion of the energy up to the second order at the optimum geometry with respect to the Cartesian coordinates partly includes the higher-order (generally up to infinite order) terms in the expansion with respect to the internal coordinates. Hence, the drastic deformation of the cyclic parts is avoided. Direct use of the expansion with respect to the internal coordinates including higher-order terms also allows us to avoid such deformation; however, cumbersome calculations become necessary, such as evaluating the higher-order derivatives of the energy

bond length   bond angle   dihedral
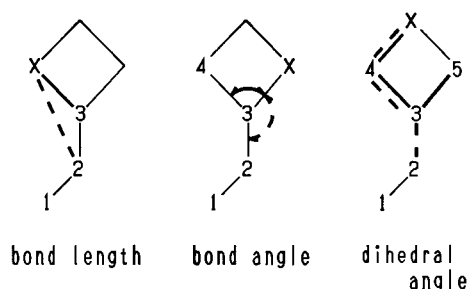   angle

Fig. 1. Recommended choice of internal coordinates. Internal coordinates, indicated by thick lines rather than broken lines, should be chosen to specify the location of the atom X.

and solving the non-linear equations. The use of the Cartesian coordinates is a simple substitute for the cumbersome calculations.

The internal coordinates defined by the atoms in the cyclic parts should be used as much as possible in order that the new position of these atoms may be determined by the new Cartesian coordinates R_C rather than the new internal coordinates R_I. The recommended choice of internal coordinates is illustrated in fig. 1. This choice would also be effective in reducing the coupling between groups $R_{IC}^{(1)}$ and $R_{IC}^{(2)}$.

3. Results and discussion

The present method is applied to the optimizations of geometries of pyridine and ethylene oxide in the ground state, and is compared with the methods where only the internal or the Cartesian coordinates are used as optimization variables. The RHF wavefunctions with the basis set of MIDI-4 [12] are used, since it is sufficient to check the performance of the optimizations by these methods. The initial geometries of these molecules are the optimum structures with the basis set of MINI-4 [12]. The internal coordinates used in the present calculations are shown in the upper-right corners of figs. 2 and 3 with solid lines. In pyridine, the atoms, except for C_3 and H_3, are constrained to take C_{2v} symmetry, so that there are twelve optimization variables. The fragment C_2H_4 in ethylene oxide is also constrained to C_{2v} symmetry, and thus the number of the optimization variables is six. The bond distances and angles depicted
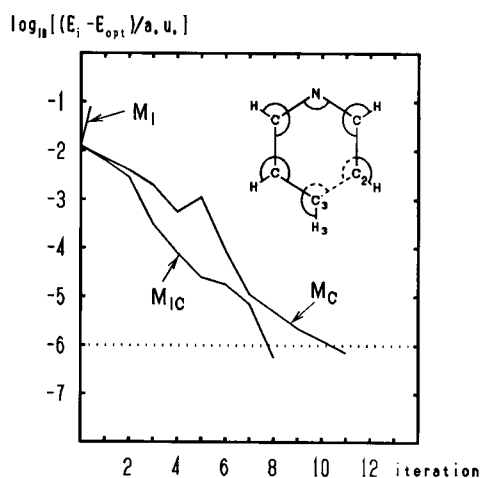
$\log_{10}[(E_i - E_{opt})/\text{a.u.}]$

Fig. 2. The change of the RHF energy of pyridine with the basis set of MIDI-4 [12] in the present optimization method M_{IC}, the method with only the internal coordinates M_I, and the method with only the Cartesian coordinates M_C. The initial geometry is optimum for the basis set of MINI-4 [12]. The optimization variables are shown in the upper-right corner with solid lines. The broken lines denote unnecessary bond distances and bond angles for specifying the locations of atoms with the internal coordinate system. The fragment without C_3 and H_3 is constrained to take C_{2v} symmetry, so that the number of independent variables is twelve. The dotted line denotes the energy difference of 10^{-6} au.

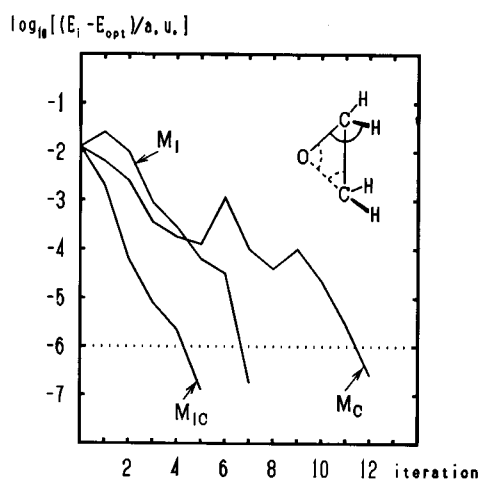$\log_{10}[(E_i - E_{opt})/\text{a.u.}]$

Fig. 3. The change of the RHF energy of ethylene oxide with the basis set of MIDI-4 [12]. The C_2H_4 fragment is constrained to take C_{2v} symmetry, so that the number of independent variables is six. For the remaining, see the legend of fig. 2.

with broken lines are unnecessary to locate the atoms in the cyclic parts, so that they are not used as the optimization variables. All the internal coordinates defined only by C, N, and O atoms belong to the first group $R_{IC}^{(1)}$, and the coordinates including hydrogen atoms belong to the second group $R_{IC}^{(2)}$. The matrix H_C in eq. (3) is initialized to the unit matrix, and the matrix H_I in eq. (2) is the same diagonal matrix as that used in GAUSSIAN 80 [13] [*1], where the diagonal elements are determined depending on the kind of atoms and values of distances or angles in the initial geometry. These matrices are improved at each iteration by the use of the rank-1 method [11].

In figs. 2 and 3, the differences of the total energies E_i's at each iteration from the energy E_{opt} at the optimum structure are plotted for pyridine and ethylene oxide, respectively. M_{IC} means the present method and $M_I(M_C)$ denotes the methods only with the internal(Cartesian) coordinates. The differences are plotted until they converge to less than 10^{-6} au, which is usually used as one of the threshold values of convergence.

In the optimization of pyridine, the method M_I results in a drastic decrease of the C_3–C_2 distance from 1.4 to 0.2 Å at the first modification geometry, which reflects the instability of the method, and further search ceased automatically. On the contrary, the present method M_{IC} and the method M_C gave the optimum structure in a stable manner after eight and eleven iterations, respectively. The present method is more efficient that the method M_C and more stable than the method M_I.

The increase of energy at the fifth iteration of the M_C method and the smaller decrease at the sixth iteration of the M_{IC} method relate, perhaps, to the use of the rank-1 rather than the rank-2 method to update the H matrices. Though the use of the rank-2 method might reduce the numbers of the iterations in both the methods, we expect that the efficiency of the M_{IC} over the M_C method would remain.

In pyridine, the number of atoms optimized by the use of the Cartesian coordinates is six out of a total

of eleven atoms, so that the efficiency of the M_{IC} method does not appear clearly. On the other hand, in ethylene oxide, the efficiency is clearer since the number is three out of seven. In both cases, the M_{IC} method converged in a smaller number of iterations than the other methods.

It is interesting that the M_I method also gave convergence. In order to clarify the reason for this, we investigated how the geometry was modified at each cycle of the optimization. At the first modification, the OCC angle increased too much, so that its change was constrained to the maximum value of 0.2 rad. At the second modification, the angle decreased too much and its change was again constrained to the maximum value. Thus, after two modifications, the angle returned to the initial value, which is almost the optimum value for the MIDI-4 basis set. The other coordinates had improved during two iterations, so that the optimization succeeded. The convergence seems to be due to good luck, and such good luck cannot be expected for a general cyclic molecule.

For some other molecules containing one or two cyclic parts, such as pyrole, N-alkyl pyridine, and several fragments of a free base porphine, we optimized their geometries by using the present method, and confirmed the efficiency and stability of the present method.

4. Concluding remarks

In this paper, we have proposed an efficient and stable method to determine the optimum structures of molecules containing cyclic parts, where the internal coordinates are classified into two groups: one group is a set of the coordinates defined only by the atoms constituting the cyclic parts; and the other is that of the remaining coordinates. The former set is improved by the use of the Cartesian coordinates, and the latter by the use of the internal coordinates. The present method was tested in the search for the optimum geometries of pyridine and ethylene oxide, which have both the cyclic and the non-cyclic parts; it has been found to be stable in contrast to the method with only the internal coordinates and more efficient than the method with only the Cartesian co-

ordinates. The key of the present method is to combine improved internal and Cartesian coordinates at each cycle of the optimization; the procedure is independent of how the improved coordinates are obtained. Therefore, the present approach is applicable to any process for obtaining the improved coordinates. We expect the present method to be useful for a further expansion of ab initio theoretical studies of molecular systems containing both the cyclic and the non-cyclic parts.

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