# The Calculation of ab Initio Molecular Geometries: Efficient Optimization by Natural Internal Coordinates and Empirical Correction by Offset Forces

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**Abstract:** Two suggestions are made to increase the efficiency and accuracy of ab initio optimization of molecular geometries. To improve the convergence of the optimization, a set of internal coordinates, the *natural valence coordinates*, is suggested. These coordinates originate from vibrational spectroscopy and reduce both harmonic and anharmonic coupling terms in the potential function as much as possible in a purely geometrical definition. The natural valence coordinates are local, eliminate most redundancies, and conform to local pseudosymmetry. Special attention has been paid to ring systems. A computer program has been included in our program system TX90 to generate the natural internal coordinates automatically. The usefulness of these coordinates is demonstrated by numerous examples of ab initio geometry optimization. Starting with a geometry preoptimized by molecular mechanics and using a simple diagonal estimate of the Hessian in conjunction with the GDIIS optimization technique, we usually achieved convergence in 8–15 steps, even for large molecules. It is demonstrated that, due to the reduction in anharmonic couplings, natural coordinates are superior to Cartesian or other simple internal coordinates, even when an accurate initial Hessian is available. Constrained optimization and the location of transition states are also discussed. The gradient optimization method has been generalized to handle redundancies; this is necessary in some complex polycyclic molecules and is illustrated on, among others, the porphine molecule. To increase the accuracy of relatively low-level calculations, empirical corrections to ab initio SCF geometries are suggested in the form of "offset forces" acting along bonds. We recommend offset forces for the most important bonds, to be used with the 4-21G(*) and the 6-31G* basis sets. Based on 130 comparisons, the mean absolute error between theoretical and experimental bond lengths is reduced this way from 0.014 to 0.005 Å.

## I. Introduction

There has been a fundamental change recently in the role that theoretical approaches play in chemistry. Due to the rapid development in computer technology and the emergence of powerful program systems, quantum chemistry has become a practical tool for the chemical community. This refers not only to the widespread semiempirical techniques but also to ab initio calculations which can be performed on widely available workstations. One of the most important applications is the determination of the equilibrium geometries of molecules. Such calculations are still fairly expensive and, except for the highest levels of theory, suffer from systematic errors. The present paper addresses these problems.

Because of the high cost of quantum chemical calculations relative to other computational tasks, it is important to develop algorithms which require as few wave function evaluations as possible. Analytic gradient techniques[1,2] have greatly increased the efficiency of geometry optimization. Analytic second derivatives[3,4] are also widely available now, but they appear to be too expensive if the only goal of the calculation is geometry optimization. It will be demonstrated in the present paper that, using only gradient information, the convergence of geometry optimization can be significantly accelerated by the appropriate choice of coordinates used to describe the positions of the nuclei. A carefully devised system of curvilinear internal coordinates proposed here has proved so useful that we suggest the name *natural internal coordinates* for them. The coordinates advocated here are a generalization of the ones suggested by us some time ago.[5] Their main disadvantages were the substantial human effort involved in specifying them for program input and the fact that they were not defined for more complex molecules. We show here how the construction of natural internal coordinates can be automated and extend their definition to include, among others, fused cycles. All our demonstrations will be ab initio results, but the method itself could be useful for semiempirical calculations on large systems.

We also consider the problem of the empirical correction of ab initio geometries. At the level applicable to larger molecules (presently Hartree–Fock wave function with modest basis sets), the geometry parameters have significant errors which are, however, fairly systematic, in particular for bond lengths. Empirical corrections to Hartree–Fock bond lengths have been in use for some time.[5,6-8] We propose here an alternative scheme in which "offset forces" are added to the calculated forces during geometry optimization. This results in a simpler and better defined correction for cyclic molecules.

## II. Theoretical Background

We are concerned here with finding a local energy minimum from a reasonably close starting geometry. The existence of multiple minima is an important and largely unsolved problem in large, flexible molecules, but it is not the subject of the present paper. A necessary condition for a minimum on the potential energy surface is that it must be a stationary point, i.e., the gradient vector **g** must vanish. Whether a stationary point is a true local minimum or a saddle point can only be determined with certainty by checking the positive definite character of the second derivative matrix. However, several of the geometry optimization methods

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0002-7863/92/1514-8191$03.00/0 

offer reasonable, although not mathematically complete, guarantees that the points they converge to are minima.

All important gradient optimization schemes are based on the Newton–Raphson method. The basis of this is an expansion of the energy in a power series in the displacement coordinates $\Delta q_i$:

$$E = E_0 + \sum g_i \Delta q_i + (1/2) \sum F_{ij} \Delta q_i \Delta q_j + \ldots$$

Truncating this expansion at the second order and minimizing with respect to $\Delta \mathbf{q}$ yields a system of linear equations which can be solved for $\Delta \mathbf{q}$:

$$\Delta \mathbf{q} = -\mathbf{F}^{-1}\mathbf{g} \qquad (1)$$

In the above formulas, $\mathbf{g}$ is the gradient vector, $g_i = (\partial E/\partial q_i)$, and $\mathbf{F}$ is the force constant matrix of Hessian, $F_{ij} = (\partial^2 E/\partial q_i \partial q_j)$. For a quadratic surface, eq 1 gives the exact solution in one step. In practice, the surface is not strictly quadratic, and eq 1 must be solved iteratively. The Newton–Raphson iteration is quadratically convergent but expensive, due to the need to evaluate the Hessian in every step. Replacing the Hessian by a reasonable approximation reduces the convergence to a linear one but is less expensive overall. Most modern methods try to use information obtained during the course of the iteration to improve the Hessian: these *variable metric* (or quasi-Newton) methods exhibit superlinear convergence. An excellent general discussion of optimization algorithms is given in Fletcher's book;[9] Schlegel[10] has also reviewed geometry optimization techniques. As the information collected during the iteration is, in general, insufficient to reconstruct the Hessian, it is difficult to assess the advantages of one algorithm over the other. The first methods widely used were the Murtagh–Sargent[11] and the Davidon–Fletcher–Powell[12] methods. More recently, the BFGS (Broyden–Fletcher–Goldfarb–Shanno) procedure[13] has been shown to perform well for geometry optimization.[14] The BERNY algorithm of Schlegel[15] has also been widely and successfully used. In most of our optimizations we have used the GDIIS technique,[16] a version of the direct inversion in the iterative subspace (DIIS) algorithm widely used to accelerate the convergence of electronic wave functions. GDIIS tries to minimize the weighted gradient norm and can thus be used to find saddle points (see section VI). Most general optimization methods include a one-dimensional search step. These methods do not work too well in quantum chemistry because the cost of calculating the energy points is not much less than that of calculating gradients. However, a one-dimensional search based on a cubic or quartic model, as suggested by Schlegel,[15] is probably very useful. No one-dimensional searches were used in the present work, but we are in the progress of incorporating a similar strategy in our program.

It is not the subject of the present paper to compare various optimization techniques. We have found, in agreement with others,[17] that the GDIIS technique used here compares favorably with BFGS. Our conclusions, however, would remain valid using a different optimization method. In our opinion, the mathematics of the single-minimum optimization problem has been explored so thoroughly by now that further significant progress can only be expected from incorporating a physical model, i.e., *structural information*, in the procedure. This simplest model serves to describe the atomic positions by a system of coordinates well adapted to the problem.

The only general requirement for the coordinates $\mathbf{q}$ is that they afford a complete description of the molecular geometry. Most optimization techniques also require that the coordinates be nonredundant, i.e., that no relation of the form $f(q_1, \ldots, q_n) = 0$ exists. (We have found recently that gradient optimization can be generalized to redundant coordinates. Examples for this will be given in section VII, but the full discussion is postponed to a forthcoming paper.)[18] Two sets of proper coordinates, which are related by a *linear* transformation, are obviously equivalent in gradient optimizations if the gradient and the Hessian are also correctly transformed. It may appear, therefore, that the only advantage of a well-chosen internal coordinate system is that it is easier to construct an empirical approximation to the Hessian in a valence-type coordinate set.[19] As the following discussion concerning the use of Cartesian coordinates shows, this reasoning[19] is not valid, however, because it overlooks the role of higher order anharmonic couplings.

The simplest choice of coordinates is Cartesian. The potential energy in Cartesian coordinates contains large couplings, both quadratic terms and higher order ones. Let us consider, for example, the internal rotation of the OH bond around the C–O bond in an alcohol. In rectilinear (Cartesian) coordinates, this rotation is accompanied by a stretching of the OH bond, causing a strong cubic coupling between the two modes. This geometry effect is absent in the curvilinear bond stretching and torsional coordinates. Due to the large couplings, a simple initial estimate of the Hessian $\mathbf{F}$ in Cartesian coordinates, such as the unit matrix sometimes used, is very poor and the algorithm needs many steps to build up a reasonable approximation to it. A better choice can be to estimate $\mathbf{F}$ from a lower level calculation or from an empirical force field (note that the latter are of course based on valence coordinates). If a good initial Hessian is used, then Cartesian coordinates should be nearly as good as any other coordinate system *for small displacements*, i.e., close to the equilibrium, where the higher order anharmonic terms are unimportant. Farther away from the equilibrium, however, the anharmonic couplings are very important. They can severely retard convergence in the early stages of iteration by preventing the agressive larger steps, particularly in systems with soft modes. They may even lead to divergence. Thus, in the general case, Cartesian coordinates are less effective even with a good initial Hessian because the higher order couplings are not accounted for. This statement will be supported by examples given in section V.

Internal coordinates (bond stretchings, valence angle bending, out of plane deformations, and torsional angles) have been used in the theory of molecular vibrations for a long time[20] and also in geometry optimization from the earliest applications of gradient theory.[1] These coordinates minimize coupling, both harmonic and anharmonic, and therefore should work better in general for geometry optimization than Cartesian coordinates. There are two principal types of internal coordinate systems. The ones we advocate originate from vibrational spectroscopy and will be described in detail in the next section.

A much simpler choice of internal coordinates is used in the "Z matrix" method implemented in several major quantum chemistry programs like, e.g., GAUSSIAN,[21] AMPAC,[22] and

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CADPAC.[23] The Z matrix is a connectivity-type definition of the molecular geometry in terms of individual bond lengths, angles, and torsional angles. Its advantage lies in its relative simplicity when it has to be set up by hand. Although the Z matrix works reasonably well in many cases, particularly in open-chain molecules, it should be realized that it was designed for input specification rather than specifically for geometry optimization. Accordingly, it is not the best choice. The treatment of rings is particularly unsatisfactory in that the last bond that closes a ring is necessarily missing. Even Cartesian coordinates may be a better choice for rings. A more versatile connectivity-type system is used in CADPAC,[23] which has the option of a special ring-closure coordinate; this alleviates the problem but still does not preclude large couplings. For individual cases, like a planar six-membered ring, special coordinates have been proposed.[17,24] Another undesirable property of the Z matrix coordinates is the nonsymmetrical treatment of valence angles around a given central atom and of the torsional angles around a given bond.

## III. Natural Internal Coordinates

We suggested a set of coordinates, based on those generally used in vibrational spectroscopy, some time ago.[5] This was used in a number of ab initio vibrational studies[8] which also included geometry optimization. We think that this system reduces the coupling of coordinates as much as possible with a general system based purely on the geometry. The subroutine that handles these coordinates has been incorporated in other programs, such as locally modified versions[25] of GAUSSIAN, and TURBOMOLE.[26] It is a fairly complex system, however, and to set it up by hand requires too much effort for the large molecules which can be calculated now. We have therefore written a program (INTC) which generates internal coordinates automatically and included it in our ab initio program system TX90.[27] A preliminary account of this program has been published earlier.[28] Independently, a similar program has been implemented[29] in the latest version of TURBOMOLE.[26]

The system of internal coordinates we are proposing is based on three fundamental principles: *locality*, *local pseudosymmetry*, and the *elimination of redundancy*. Locality simply reflects the basic chemical picture of a molecule as being built out of bonds and groups of atoms fairly independent of the rest. Approximate local symmetry is used to eliminate local redundancies and to reduce couplings between coordinates centered on the same atom. However, global symmetry that would possibly connect coordinates at two far ends of a molecule is emphatically avoided. Our coordinates are best suited for organic molecules with a normal bonding pattern. They are not specifically adapted to unusual bonding situations, such as those occurring in transition states or in excited states. Nevertheless, they probably perform as well as any other system of coordinates for unusual bonding situations too, and better for spectator groups. It is clear that the present system is not applicable in every possible situation, and we are working on extending it. In particular, at present it is necessary to use redundant coordinates in some cases.

In the following points we summarize the principles used to define the *natural internal coordinates*. Instead of giving detailed descriptions for various individual cases, we illustrate these principles in Table I for a few molecules, deliberately chosen to include several types of bonding situations. We also refer to our earlier paper,[5] which is extended and slightly modified by the present definition. It is also likely that minor differences in the definition of the coordinates would not change significantly the convergence behavior of geometry optimization. For simple linear chains and isolated rings, the coordinate system used is rigorously defined and is essentially the same as that in ref 5. We also illustrate extensions to more complicated systems. However, we do not define our coordinates in all possible situations, as it is possible that, as experience accumulates, our definitions may change slightly.

1. The first step in the construction of natural coordinates is a *topological* investigation. For each atom, the coordination number (number of neighbors connected to it) is established. Atoms with one connection only are terminal atoms. An important step is the location of rings. After this, the nonterminal atoms form two basic groups, nonring (chain) atoms and ring atoms. At present, the maximum coordination number is 6 for chain atoms and, except for a few special cases like a silatrane type structure, 4 for ring atoms.

Around each atom as a center, *pseudosymmetry* is defined in the following way. Terminal neighbors are considered as one set of equivalent atoms, nonterminal neighbors (connecting to the skeleton of the molecule) as another set of equivalent atoms. If the center is a ring atom, its ring neighbors form one set, and the substituents, whether of the same type or not, another set. For simplicity, let us consider only the two most important cases of four and three neighbors, respectively. A tetracoordinated center this way can have $T_d$ symmetry (all neighbors of the same type in the above sense), $C_{3v}$ symmetry (one terminal and three nonterminal neighbors or the reverse), or $C_{2v}$ symmetry (two neighbors of each of the two types). $C_{3v}$ symmetry coordinates are used also in the $T_d$ case. For a tricoordinated atom the symmetry can be $C_{3v}$ or $C_{2v}$, but the coordinates will be different depending on whether the center is planar (quasi-planar) or not (see below). Pseudosymmetry is the basis of forming angle deformational coordinates below. Ring atoms are handled by special ring coordinates (points 5 and 6) and, consequently, $C_{2v}$ symmetry is used for constructing the coordinates of the substituents on the ring atom (there can be one or two of them).

2. Bonds are described by *individual* stretching coordinates. This is suggested by the generally low coupling between bonds (even in conjugated systems) and the fact that anharmonicity can be described in the most compact form in terms of individual bonds. Note that individual stretchings are used also in rings (see point 4 below).

3. For bond angle deformations, the individual coordinates are bendings[20] in the general case and linear bendings[20] for linear or quasi-linear groups. From the individual coordinates, composite symmetrized coordinates are formed on the basis of *idealized local symmetry* described in 1. For example, for an $sp^3$ methylene group, $CH_2$, $C_{2v}$ symmetry coordinates[20] are used which describe the "scissoring", "rocking", "wagging", and "twisting" motions (see $q_{35}$–$q_{38}$ and $q_{39}$–$q_{42}$ for the methylene groups in the three-membered-ring part of the spiro compound **1a** in Table I). Similarly, the definition of the methyl coordinates is based on $C_{3v}$ symmetry (see $q_{43}$–$q_{47}$ for the methyl group attached to the five-membered ring in Table I). In the tricoordinated case one has to distinguish the planar or quasi-planar configuration from the pyramidal one. In the former case out-of-plane type bendings[20] are also needed, and combinations are again formed according to symmetry.[5] Examples of the planar case with $C_{2v}$ local pseudosymmetry are given in Table I by the CH and C–Me rockings (in-plane bending combinations) and waggings (out-of-plane bending) of model **1a**, see $q_{27}$–$q_{34}$.

The use of linear combinations rather than individual bendings is a very important feature: the redundancy of angles around a central atom is removed this way; also, the couplings in the force constant matrix between these coordinates are relatively small even in the absence of true symmetry (the latter would render all couplings between the above types of coordinates zero by symmetry). We note parenthetically that the coordinates used are not strictly orthogonal to the exact redundancies. There is no such theoretical or practical requirement, although the redundancy should be roughly orthogonal to the space of the co-

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**Table I.** Natural Internal Coordinates for the Model Molecules in Figure 1[a]

4-Methylspiro[2.4]hepta-2,4-diene (**1a**)

$q_1$–$q_{19}$: Individual Bond Stretchings. $q_{20}$–$q_{23}$: Five-Membered Ring Coordinates as Defined by Eq 2 in the Text

| descr | coeff | type | atoms |
|---|---|---|---|
| $q_{24}$ | +1 | bend | 2, 6, 1 |
| ring- | +1 | | 5, 6, 1 |
| ring | −1 | | 2, 7, 1 |
| rock | −1 | | 5, 7, 1 |
| $q_{25}$ | +1 | bend | 2, 6, 1 |
| ring- | −1 | | 5, 6, 1 |
| ring | +1 | | 2, 7, 1 |
| wagg | −1 | | 5, 7, 1 |
| $q_{26}$ | +1 | bend | 2, 6, 1 |
| ring- | −1 | | 5, 6, 1 |
| ring | −1 | | 2, 7, 1 |
| twist | +1 | | 5, 7, 1 |
| $q_{27}$ | 1 | bend | 1, 9, 2 |
| CH rock | −1 | | 3, 9, 2 |
| $q_{28}$ | 1 | out | 9, 1, 3, 2 |
| CH wag | | | |
| $q_{29}$ | 1 | bend | 2, 10, 3 |
| CH rock | −1 | | 4, 10, 3 |
| $q_{30}$ | 1 | out | 10, 2, 4, 3 |
| CH wag | | | |
| $q_{31}$ | 1 | bend | 5, 8, 4 |
| C–Me rock | −1 | | 3, 8, 4 |
| $q_{32}$ | 1 | out | 8, 5, 3, 4 |
| C–Me wag | | | |
| $q_{33}$ | 1 | bend | 1, 11, 5 |
| CH rock | −1 | | 4, 11, 5 |
| $q_{34}$ | 1 | out | 11, 1, 4, 5 |
| CH wag | | | |
| $q_{35}$ | 4 | bend | 12, 13, 6 |
| CH2 | −1 | | 12, 1, 6 |
| sciss | −1 | | 12, 7, 6 |
| | −1 | | 13, 1, 6 |
| | −1 | | 13, 7, 6 |
| $q_{36}$ | 1 | bend | 12, 1, 6 |
| CH2 | 1 | | 12, 7, 6 |
| rock | −1 | | 13, 1, 6 |
| | −1 | | 13, 7, 6 |
| $q_{37}$ | 1 | bend | 12, 1, 6 |
| CH2 | −1 | | 12, 7, 6 |
| wag | 1 | | 13, 1, 6 |
| | −1 | | 13, 7, 6 |
| $q_{38}$ | 1 | bend | 12, 1, 6 |
| CH2 | −1 | | 12, 7, 6 |
| twist | −1 | | 13, 1, 6 |
| | 1 | | 13, 7, 6 |
| $q_{39}$–$q_{42}$: CH2 deformations around C7, analogous to $q_{35}$–$q_{38}$ at C6 above | | | |
| $q_{43}$ | 1 | bend | 17, 18, 8 |
| CH3 | 1 | | 16, 18, 8 |
| s def | 1 | | 16, 17, 8 |
| | −1 | | 4, 16, 8 |
| | −1 | | 4, 17, 8 |
| | −1 | | 4, 18, 8 |
| $q_{44}$ | 2 | bend | 17, 18, 8 |
| CH3 | −1 | | 16, 18, 8 |
| as def | −1 | | 16, 17, 8 |
| $q_{45}$ | 1 | bend | 16, 18, 8 |
| CH3 | −1 | | 16, 17, 8 |
| as def′ | | | |
| $q_{46}$ | 2 | bend | 4, 16, 8 |
| CH3 | −1 | | 4, 17, 8 |
| rock | −1 | | 4, 18, 8 |
| $q_{47}$ | 1 | bend | 4, 17, 8 |
| CH3 | −1 | | 4, 18, 8 |
| rock′ | | | |
| $q_{48}$ | 1 | tors | 16, 8, 4, 3 |
| CH3 | 1 | | 17, 8, 4, 3 |
| torsion | 1 | | 18, 8, 4, 3 |
| | 1 | | 16, 8, 4, 5 |
| | 1 | | 17, 8, 4, 5 |
| | 1 | | 18, 8, 4, 5 |

Skeleton of Bicyclooctane (**1b**)[b]

$q_1$ – $q_9$: Individual Bond Stretchings. $q_{10}$–$q_{15}$ and $q_{16}$, $q_{17}$: Six-Membered Ring and Four-Membered Ring Coordinates, Respectively, as Defined by Eq 2 in the Text

| descr | coeff | type | atoms |
|---|---|---|---|
| $q_{18}$ | 1 | tors | 4, 5, 6, 7 |
| butterfly | −1 | | 8, 5, 6, 1 |

Skeleton of Propellane (**1c**)[c]

$q_1$–$q_{10}$: Individual Stretchings. $q_{11}$–$q_{16}$: Four-Membered Ring Coordinates as Defined by Eq 2

| descr | coeff | type | atoms | descr | coeff | type | atoms |
|---|---|---|---|---|---|---|---|
| $q_{17}$ | 2 | tors | 2, 3, 4, 5 | $q_{18}$ | 1 | tors | 2, 3, 4, 7 |
| | −2 | | 6, 3, 4, 1 | | −1 | | 8, 3, 4, 1 |
| | −1 | | 2, 3, 4, 7 | | −1 | | 8, 3, 4, 5 |
| | +1 | | 8, 3, 4, 1 | | +1 | | 6, 3, 4, 7 |
| | −1 | | 8, 3, 4, 5 | | | | |
| | +1 | | 6, 3, 4, 7 | | | | |

Butyrolactam Dimer (**1d**)

Only the Coordinates Describing the Relative Motions of the Subunits Are Listed

| descr | coeff | type | atoms | descr | coeff | type | atoms |
|---|---|---|---|---|---|---|---|
| $q_{67}$ | 1 | stre | 14, 6 | $q_{70}$ | 1 | tors | 12, 13, 6, 14 |
| $q_{68}$ | 1 | stre | 13, 12 | | −1 | | 13, 6, 14, 12 |
| | | | | | 1 | | 6, 14, 12, 13 |
| $q_{69}$ | 1 | bend | 6, 12, 13 | | −1 | | 14, 12, 13, 6 |
| | −1 | | 14, 13, 6 | | | | |
| | 1 | | 12, 6, 14 | $q_{71}$ | 1 | tors | 2, 6, 13, 12 |
| | −1 | | 13, 14, 12 | | −1 | | 1, 13, 6, 14 |
| | | | | $q_{72}$ | 1 | tors | 8, 12, 14, 6 |
| | | | | | −1 | | 7, 14, 12, 13 |

[a] Coordinates were generated by the INTC routine of TX90 (ref 27), their format was edited for this paper. In general, a coordinate is the linear combination of several individual coordinates, the latter of the type used in vibrational spectroscopy, see, e.g., ref 20. The individuals are defined by type in column 3 and the atoms participating, column 4 (note that for bend types, the last index refers to the central atom). The coefficients as listed in column 2 are relative values only, they are normalized in the program. [b] Relative motion of the two rings. [c] Relative motions of the rings.

ordinates, to avoid close linear dependencies.

The composite bending coordinates are normalized by the spectroscopic convention, $(\sum c_i^2)^{-1/2}$. Although we avoid global symmetry in the construction of the coordinates, the program tries to choose the orientation[20] of degenerate type coordinates (e.g., in the $C_{3v}$ case) so that symmetry is maintained.

4. The relative torsional motion around an X–Y bond is described by the sum of all torsional angles $A_i$–X–Y–$B_j$. Normalization here, contrary to the bendings, is $1/n$, which is more consistent with the form of potential for torsions. It is important to define torsions in this symmetrical way, as internal rotation is frequently a source of convergence difficulties in geometry optimization. A minor complication with torsions is their multivalued nature: a small change during optimization may appear as a sudden jump if the zone limit is crossed. This is recognized by the program and handled appropriately.

5. Rings, except for macrocycles, are considered as a local grouping, and in the construction of the coordinates use is made of the *idealized highest symmetry*, $D_{nh}$. The treatment of rings is the weakest point in many optimization procedures, and we think that the following scheme is one of the most important features of the present method. In the original formulation[5] we gave explicit definitions for rings of up to six atoms only. The following is a general definition for rings of any size. However, for large macrocycles, we recommend the use of redundant internal coordinates.

An $n$-membered ring has $3n - 6$ degrees of freedom which we describe by $n$ individual stretchings, $n - 3$ symmetrized bendings, and $n - 3$ symmetrized torsions. The symmetrized deformational coordinates are obtained from group theory as

$$S_m^a = \sum_{k=1}^{n} \cos\{(k-1)m2\pi/n\}q_k \qquad (2a)$$

$$S_m^b = \sum_{k=1}^{n} \sin\{(k-1)m2\pi/n\}q_k \qquad (2b)$$

where $q_k$ denotes the individual bendings or torsions, respectively, and $m$ refers to the symmetry species under the $D_{nh}$ point group; $m = 2,[n/2]$, where $[n/2]$ is the integer part of $n/2$. The values $m = 0$ and 1 correspond to redundancies and are excluded.

6. Polycyclic systems can present the greatest difficulties, and in the general case we have to use redundant coordinates (section VII). However, in the most important cases we can exclude redundancy as described in the following examples.

(a) Fused rings sharing one edge, such as naphthalene or phenanthrene, or in general, [*n.m.*0] type bicyclic systems, require (beyond the internal coordinates for each ring separately as described in point 5) a special coordinate that describes the relative motion of two adjacent rings. We call this coordinate "butterfly", and it is defined as the difference of two appropriate torsions around the annelation bond. It is demonstrated by the example of $q_{18}$ for bicyclooctane in Table I.

(b) Bicyclic systems of the general [*n.m.k*] type with $k$ (greater than zero) atoms in the bridge, like norbornane (bicyclo[2.2.1]-heptane), are more complicated. We recommend using the ring coordinates of the two rings, with $(n + k + 2)$ and $(m + k + 2)$ atoms, in the norbornane case two five-membered rings. This introduces redundancy and will be discussed in section VII.

(c) For propellane type tricyclic systems there are two special coordinates describing the relative orientation of the ring planes. These are constructed as appropriate combinations of torsional coordinates around the common edge, using $C_3$ symmetry around that bond. An example is given by $q_{17}$ and $q_{18}$ for [2.2.2]propellane in Table I. We used this system with good success also in a silatrane derivative, defining the Si···N partial bond as a true bond.

(d) In spiro systems the relative motions of the two rings can easily be described by coordinates of the regular type rocking, wagging, and twisting, defined around the spiro center atom. For the spiro compound in Table I, these are given by $q_{24}$, $q_{25}$, and $q_{26}$.

For polycycles more complicated than the cases listed above, the simplest solution is probably to accept redundant coordinates, after excluding the local angle and ring redundancies.

7. Supermolecules, ensembles of molecules connected by relatively weak bonds like H-bonds, need special treatment.

First, the obvious task is to recognize the hydrogen bond. In our INTC routine this is now controlled by the input. (As a special option, any atom pair can be defined as bonded.) The less obvious second question is to find the "natural" coordinates. At present we can handle two cases.

(a) In the case of one H-bond, the system is treated simply as a supermolecule with the regular coordinates around the H-bond. Obviously, the X–H···Y bending and especially the torsion around H···Y are extremely loose coordinates. This may necessitate special optimization techniques like constrained optimization along the soft mode as discussed in section VI.

(b) A fairly important situation is two H-bonds forming a ring as in the case of the butyrolactam dimer, Figure 1d. One possible choice would be to use the eight-membered ring that appears to be due to the H-bonds, but this leads to extremely loose coordinates. We have found that the system as given in Table I performs quite well. In essence, the relative orientation of the two submolecules is described by the angular coordinates of the four-membered ring formed by the oxygens and the hydrogens and two butterfly type coordinates.

The above considerations assume weak but still reasonable bondings between the subunits. The extreme case of almost independent molecules within a cluster, where the individual molecules undergo large-amplitude translational and rotational motion, needs special techniques as discussed recently by King.[30]

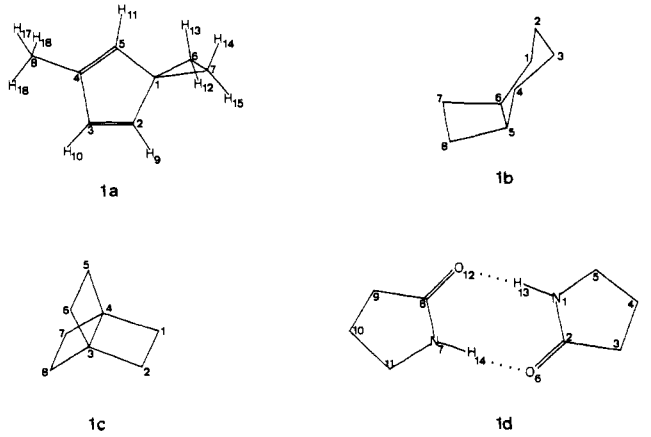


**Figure 1.** Numbering of atoms in the models used to illustrate the definition of natural internal coordinates in Table I. Hydrogens are indicated only if used in Table I. **1a**: 4-Methylspiro[2.4]hepta-2,4-diene. **1b**: Bicyclo[4.2.0]octane. **1c**: [2.2.2]Propellane. **1d**: The hydrogen-bonded dimer of γ-butyrolactam.

## IV. Computational Details

This section summarizes the computational details used to obtain the examples in the next section. Based on the principles outlined above we have now a well automated, easy-to-use scheme for large-scale ab initio geometry optimizations as part of the program system TX90.[27] The natural internal coordinates are generated by the INTC subroutine in a format read by BMAT, the subroutine that makes the transformation of the gradient from Cartesian to internal coordinates. This may be of interest because the original BMAT[31] has been incorporated into several major quantum chemistry program systems. INTC also produces a guess of diagonal force constants, taken simply from basic molecules with known force fields. If a better estimate (e.g., a semiempirical force field) is available, a more general Hessian can be specified. However, in all the examples in this paper the default simple diagonal Hessian guess was used, in conjunction with the GDIIS optimization technique.[16] In some cases we tried to combine GDIIS with the BFGS updating method,[13] but no further improvement was obtained.

The starting geometries were obtained in almost all cases by PCMODEL,[32] a commercial program that uses the MMX force field of Ga-

(30) King, H. F. *J. Phys. Chem.* **1990**, *94*, 5617.
(31) Meyer, W.; Pulay, P. *MOLPRO*, Stuttgart-München, 1969.

Table II. Examples for the Convergence of Geometry Optimizations Using Natural Internal Coordinates[a]

| molecule[b] | notes[c] | cycle | SCF energy[d] | max force[e] | max coord change[f] |
|---|---|---|---|---|---|
| *N-tert*-butyl-2-propen-1-imine (**2a**) | $n$ = 34 ($C_s$) | 1 | −326.383 832 | 0.1500 | 0.1500 |
| | std | 6 | −326.394 729 | 0.0008 | 0.0004 |
| 4-methylspiro[2.4]hepta-2,4-diene (**1a**) | $n$ = 48 | 1 | −304.829 079 | 0.9126 | 0.3000 |
| | STO-3G, no offs | 7 | −304.991 912 | 0.0044 | 0.0009 |
| 1,4,5-trihydroxyanthraquinone (**2b**) | $n$ = 51 | 1 | −907.271 418 | 0.2945 | 0.2667 |
| | 4-21(*), no offs | 9 | −907.314 952 | 0.0023 | 0.0009 |
| *cis*-bicyclo[4.2.0]octane (**1b**) | $n$ = 60 | 1 | −310.429 522 | 0.1412 | 0.3000 |
| | std | 8 | −310.441 510 | 0.0001 | 0.0001 |
| oxocane, conformer TC (**2c**) | $n$ = 60 | 1 | −347.350 152 | 0.0936 | 0.0681 |
| | std | 8 | −347.358 044 | 0.0003 | 0.0021 |
| 4-hydroxybenzoic acid, 4-carboxyphenyl ester (**2d**) | $n$ = 81 | 1 | −908.448 124 | 0.2149 | 0.3000 |
| | std | 13 | −908.478 933 | 0.0002 | 0.0052 |
| retinal, protonated Schiff base (**2e**) | $n$ = 147 | 1 | −827.331 265 | 0.4340 | 0.3000 |
| | std | 14 | −827.335 300 | 0.0007 | 0.0009 |
| bicyclo[2.2.1]heptane (norbornane) (**2f**) set A[g] | $n$ = 15 ($C_{2v}$) | 1 | −272.052 650 | 0.1842 | 0.1842 |
| | 6-31G*, no offs | 8 | −272.061 190 | 0.0004 | 0.0001 |
| γ-butyrolactam, H-bonded dimer (**1d**) | $n$ = 72[g] | 1 | −568.598 605 | 0.4156 | 0.3000 |
| | 4-21(*), no offs | 15 | −568.626 923 | 0.0003 | 0.0073 |
| bicyclo[2.2.1]heptane (norbornane) (**2f**)[i] set B[g] | $n$ = 15 ($C_{2v}$) | 1 | −272.052 650 | 0.1693 | 0.0583 |
| | 6-31G*, no offs | 5 | −272.061 192 | 0.0006 | 0.0004 |
| porphine (**2g**)[i] | $n$ = 37 ($C_{2v}$)[h] | 1 | −981.241 288 | 0.4303 | 0.1209 |
| | 4-21G(*), no offs | 8 | −981.278 110 | 0.0030 | 0.0008 |

[a] Besides the last converged cycle, characteristics for the first step are also listed to indicate the distance from the optimum. The starting geometries were taken from molecular mechanics (refs 32, 33) optimization, using the commercial program PCMODEL (ref 32). [b] See also the figures. [c] $n$ gives the number of degrees of freedom (variable parameters); unless otherwise indicated, no symmetry was applied. The standard case is indicated by std: 4-21G(*) basis used with offset forces (see text). In other cases, the basis set is given and no offs stands for no offset forces used. [d] Energy in atomic units; when using offset forces, this is slightly different from the SCF minimum. [e] Along the internal coordinates, in units of aJ/Å or aJ/rad; note that in atomic units these figures would be smaller by almost an order of magnitude. [f] In angstroms or radians; maximum change limited to 0.3. [g] Two different coordinate systems tested, see text. [h] For the present test a simple RHF wave function was used, and that gives this symmetry; note, however, that an MCSCF wave function may be necessary to obtain the correct electronic structure. [i] Optimizations using redundant coordinates.

jewski and Gilbert. MMX is based on the MM2 force field of Allinger and co-workers.[33] The graphical input in PCMODEL, as well as the easy visualization of the results, proved very important in improving productivity and avoiding errors. Our input also has interfaces to several major quantum chemistry programs, e.g., AMPAC.[22] We have found that the MMX geometries are very good in most cases but still far enough from the ab initio ones to serve as realistic tests of the optimization procedure. In general, the deviation between the MMX and the final optimized ab initio geometries was a few hundredths of an angstrom for bond lengths, a few degrees for bond angles, and up to 10° and more for torsions.

Except for the transition state for the dissociation of the *tert*-butoxy radical, we used the simple restricted Hartree–Fock (RHF) theory. In the examples of sections V–VII, the only purpose was to study the convergence behavior of the geometry optimization; the quality of basis sets is ad hoc, varying from the simplest STO-3G to the large 6-311G**.[34] Otherwise, however, we consider two pairs of basis sets as especially suitable for the purpose of large-scale geometry optimizations. These were used consistently in the determination of bond lengths in section VIII. Both are relatively simple and of the split-valence type. The 4-21G(*) set is the set that we consider as standard for use on first-row atoms in large molecules. This is the original 4-21G basis,[5] augmented with a set of five d functions of exponent 0.8, applied uniformly on nitrogen, oxygen, and fluorine (but not on carbon). The use of d functions on atoms with lone pairs is justified by the well-known experience that they improve the description of angle deformations. For second-row elements the corresponding basis set we use is the 3-3-21G(*) set (with 6-component d functions, consistent with the original definition[35]). In special cases, especially in strained systems, use of the larger 6-31G* basis set[36] may be necessary. All optimizations in section VIII were carried out with both the 4-21G(*) and the 6-31G* sets.

## V. Examples of Geometry Optimization

Several test examples of optimization are given in Table II. Beside the converged last step, characteristics of the starting first step are also listed; this gives an estimate of what distance the optimization had to cover. Details of the optimization history are available upon request from the authors. As convergence criterion the maximum value of the following quantity proved useful: $\Delta E_i = {}^1/_2\varphi_i\Delta q_i$, where $\varphi$ is the force, and $\Delta q$ is the coordinate change. In the examples given, a threshold of $10^{-6}$ aJ was used. This is a fairly strict limit and may not always be necessary. With this criterion, the total energy is usually accurate to better than $10^{-5}$ au. Note that in most cases we applied empirical corrections to the forces acting along bond stretching coordinates (see section VIII), and therefore it is the *corrected SCF energy*, not the SCF energy itself, which is minimum at the converged geometry.

The first example in Table II, a propenimine derivative (**2a**), was included to show a typical "easy" case of a relatively small and, due to the planarity constraint for the conjugated chain, fairly rigid molecule. Convergence in six steps is, in fact, not surprising. The next example, the spiro compound **1a** that was the prototype to show the basic types of natural coordinates in Table I, would be a very difficult case with traditional techniques: although it is a rigid system, its topology is complex. The rapid convergence we obtained for this complicated ring structure can definitely be ascribed to the use of the natural coordinates. The third example, an anthraquinone derivative (**2b**), was inspired by the thorough study of optimization techniques at the semiempirical level by Cummins and Gready.[17] These authors found this molecule to

(32) *PCMODEL*, Molecular Modeling Software. Serena Software, Box 3076, Bloomington, IN, 47402-3076. Copyright 1987, 1988, 1989, 1990.

(33) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551 and references therein.

(34) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(35) (a) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (b) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(36) (a) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

**Table III.** Comparison of Geometry Optimization in Internal and Cartesian Coordinates

| | natural internal coordinates | | | | | Cartesian coordinates | | |
|---|---|---|---|---|---|---|---|---|
| molecule | basis set | $N^a$ | $f^b$ | $\Delta q^c$ | $E_{tot}$ (au) | basis | $N^a$ | ref |
| acrolein | 4-21G(*) | 6 | 0.0005 | 0.0002 | −190.363 828 | *d* | 26 | 14 |
| start[e] | | | 0.8378 | 0.0931 | −190.349 607 | | | |
| ethanol | STO-3G | 5 | 0.0007 | 0.0004 | −152.132 673 | STO-3G | 23 | 40 |
| start | | | 0.5179 | 0.0968 | −152.125 212 | | | |
| ACTHCP[f] | 3-21G | 13 | 0.0004 | 0.0016 | −844.540 842 | STO-3G | 90 | 40 |
| start | | | 0.4275 | 0.2292 | −844.514 066 | | | |
| Acygly11[g] | STO-3G | 8 | 0.0003 | 0.0072 | −428.943 235 | STO-3G | 66 | 40 |
| start | | | 0.6257 | 0.2078 | −428.921 062 | | | |
| Acygly11[g] | 3-21G | 9 | 0.0002 | 0.0083 | −432.194 509 | STO-3G | 66 | 40 |
| start | | | 0.3448 | 0.1181 | −432.185 115 | | | |

[a] Number of steps required for convergence. In the Cartesian case, if several optimizations were quoted, the lower value is shown. [b] Maximum internal force (in aJ/Å or aJ/rad) in the last step, and (below) maximum internal force in the first step. [c] Maximum geometry change (in Å or rad) in the last step, and (below) maximum geometry change in the first step. [d] The quantum chemical method is not specified in ref 14, but it is believed to be a semiempirical technique. [e] For acrolein, PCMODEL gave an improbably short C–C single bond distance, 1.357 Å. We believe that this is due to a program error, as the result depends on the numbering of the atoms. [f] $C_5H_6N_2O_2S$, a bicyclic sulfur-containing imide, see ref 40. [g] Acetylglycine, see ref 40. The data shown are for the extended conformer; it is not clear what conformer is shown in ref 40.

be a difficult case: no convergence could be achieved with Z matrix coordinates, and 53 steps were needed with their special coordinates. We obtained very strict convergence in just nine steps, showing that the natural coordinates are well adapted to the system. This molecule is planar and quite rigid. A similar but more flexible, nonplanar system can be a greater challenge. A case of the latter type is bicyclooctane (**1b**). Still, convergence is rapid in just eight steps. The next example, oxocane (**2c**), is a very flexible eight-membered ring. Here we show only one of its conformers, the twist-chair form. An experimental–theoretical study of its conformations will be published separately.[37] Convergence again is achieved in eight steps; the fact that the MMX geometry is a good approximation of the ab initio one helps, of course.

Convergence for the ester dimer of *p*-hydroxybenzoic acid (**2d**) is rather slow, in 13 steps. Details of the process not reproduced here show that the primary parameters converge rapidly, and the second half of the cycles is spent optimizing torsions, particularly the one around the oxygen in the ester bridge and the aromatic carbon, see Figure 2. This case is difficult because the potential is flat and the three single-bond torsions in the ester bridge are strongly coupled. A more sophisticated line search algorithm could accelerate convergence in such cases. Clearly, the physical significance of the minimum energy geometry becomes questionable for such very flat potential surfaces. In this case, our starting MMX geometry differed from the final one by 8° for the C–O–C angle, and by 30° for the C(phenyl)–C(carbonyl) torsion.

Our last regular example is the protonated Schiff base of retinal (**2e**). This is a molecule with 147 independent geometry parameters, several of them soft torsional modes. Considering the large (35°) changes in some torsional angles, convergence in 14 steps is quite reasonable.

Two further, more experimental results are also given in Table II. One of them is the set A calculation for norbornene (bicyclo[2.2.1]heptane). As explained in section III, we have no unique nonredundant ring coordinates for such a system. In set A we introduced an imaginary bond between the bridgehead atoms, creating a propellane-like system. This scheme worked well, needing eight steps for convergence. However, the use of redundant coordinates (set B, discussed in section VII) seems preferable. Another example illustrates the handling of intermolecular hydrogen bonds as discussed in section III. The model is the hydrogen-bonded dimer of butyrolactam (**1d**), brought to our attention by Professor S. Saebø.[38] This is a challenging system because the relative motion of the two monomers is very floppy. In particular, the force constants corresponding to the relative orientation of the monomers (coordinates $q_{69}$ to $q_{72}$ in Table I) may be of the order of $10^{-2}$ aJ/rad$^2$. Convergence was obtained

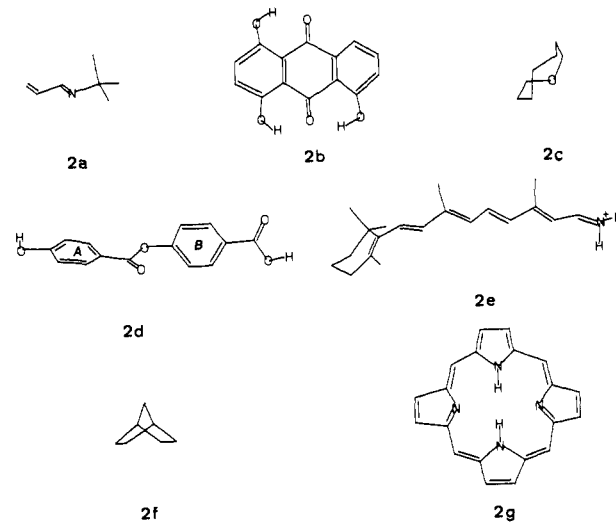


**Figure 2.** Molecules used to study the convergence behavior of geometry optimization (Tables II and III). **2a**: *N-tert*-butyl-2-propen-1-imine. **2b**: 1,4,5-Trihydroxyanthraquinone. **2c**: Oxocane, a twist-chair conformer. **2d**: 4-Hydroxybenzoic acid, 4-carboxyphenyl ester. **2e**: The protonated Schiff base of retinal. **2f**: Bicyclo[2.2.1]heptane (norbornane). **2g**: Porphine.

in an acceptable 15 steps. However, details not listed show that the last six steps were spent in optimizing the same coordinate. This again points to possible improvements in our interpolated line search algorithm. The final geometry has $C_2$ symmetry, although this was not imposed. There are large differences in this case between the starting MMX and the final geometry: the O···H distances change by 0.2 Å, and the angles and torsions in the four-membered ring change by about 10° and 20°, respectively.

**Comparison with Cartesian Coordinates.** Cartesian coordinates are much simpler than interval coordinates, and it has been claimed that they are completely equivalent[14,19,39] or even superior[40] to them. As discussed in section II, Cartesian coordinates are equivalent to internal coordinates only for very small displacements, i.e., near to equilibrium. Baker and Hehre[40] identify internal coordinates with the Z matrix coordinates. With this limited interpretation, they are correct that Cartesian coordinates are superior to the latter, for rigid rings. Even so, for chain molecules, where the performance of Z matrix coordinates is adequate, this is no longer true. In the general case, however, we are convinced that Cartesian coordinates cannot compete with a *well selected* system of internal coordinates, like the natural

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(38) Saebø, S., Mississippi State University, private communication.
(39) Head, J. D. *J. Comput. Chem.* **1990**, *11*, 67.
(40) Baker, J.; Hehre, W. J. *J. Comput. Chem.* **1991**, *12*, 606.

Table IV. Determination of a Transition State for the *tert*-Butoxy Radical[a]

1. Constrained Optimizations along the Reaction Coordinate $Q$ = C1···C2 (Theory: UHF, 4-21G)

| fixed value of $Q$ (Å) | cycle $i$ | energy (au) $E$ | max force (aJ/Å)[b] $\varphi$ | max coord. change[b] (Å or rad) $\Delta q$ | selected geometry parameters (Å or deg) C2–O3 $R2$ | O3 out[c] $\theta$ | Cl···C2 $Q$ |
|---|---|---|---|---|---|---|---|
| 2.037 | 1 | −230.973 515 | 0.1810 | 0.1717 | | | |
| | 7 | −230.993 852 | 0.0001 | 0.0006 | 1.359 | 36.3 | *d* |
| 1.837 | 5 | −231.017 429 | 0.0022 | 0.0016 | 1.434 | 47.9 | *d* |
| 2.237 | 8 | −230.988 263 | 0.0020 | 0.0010 | 1.277 | 20.9 | *d* |

2. Unconstrained Optimization Started with the Geometry Obtained for $Q$ = 2.237 Å, Above: The Last Step is the Transition State (UHF, 4-21G)

| $i$ | $E$ | $\varphi$ | $\Delta q$ | $R2$ | $\theta$ | $Q$ |
|---|---|---|---|---|---|---|
| 1 | −230.988 263 | 0.0270 | 0.0135 | | | |
| 7 | −230.988 176 | 0.0003 | 0.0004 | 1.286 | 22.6 | 2.210 |

3. Unconstrained Reoptimizations of the Transition State at Higher Levels of Theory

| theory | $i$ | $E$ | $\varphi$ | $\Delta q$ | $R2$ | $\theta$ | $Q$ |
|---|---|---|---|---|---|---|---|
| UNO-CAS | 1 | −231.012 518 | 0.1000 | 0.0494 | | | |
| 4-21G | 7 | −231.011 431 | 0.0008 | 0.0005 | 1.288 | 25.5 | 2.155 |
| UNO-CAS | 1 | −231.514 031 | 0.5052 | 0.0622 | | | |
| 6-31G* | 8 | −231.512 751 | 0.0006 | 0.0007 | 1.259 | 28.2 | 2.067 |
| UNO-CAS | 1 | −231.574 861 | 0.0557 | 0.0062 | | | |
| 6-311G** | 7 | −231.574 874 | 0.0003 | 0.0007 | 1.256 | 28.7 | 2.052 |

[a] See Figure 3 (C2 is the central carbon, C1 is being moved). [b] Excluding the force along the frozen coordinate; absolute values given. [c] The angle between bond C2–O3 and plane C5–C2–C4 (Figure 3), indicating the pyramidal character of the grouping. [d] Constrained reaction coordinate, see first column.

coordinates. We optimized some of the more difficult cases given in refs 14 and 40 using natural coordinates and compare the convergence with that of the Cartesian coordinates in Table III. The results in this table are not fully conclusive, as the starting geometries are not specified in refs 14 and 40, the initial Hessian is different, and in some cases our quantum chemical method is different. Nevertheless, it is apparent that all these difficult cases are handled quite efficiently by natural internal coordinates. To characterize the quality of the starting geometry, we have included the maximum force and geometry change components and the total energy in the first step. Table II offers further well-defined cases for future comparison.

## VI. Constrained Optimization and Transition States

One of the advantages of internal coordinates is that constraints (which are naturally formulated in internal coordinates) can easily be imposed. This can be done only in an approximate way by using projection operators if the optimization itself is carried out in Cartesian coordinates.[2,41]

Constraints can be introduced for several purposes. In systems with an extremely weak coordinate the surface may be so anharmonic that a minimum can be found only by fixing the floppy coordinate at several values and reoptimizing the remaining coordinates at each of these values. A more important application is the search for transition states. If the reaction coordinate can be approximately identified in advance, then optimizing the structure along the reaction path, at fixed values of the putative reaction coordinate, offers a straightforward way of finding the transition structure.[19] As discussed in section II, the GDIIS procedure[16] can be used to find transition states, if the search for stationary points is started in the vicinity of such a saddle point. Constrained optimization with reaction coordinate driving is usually successful to locate the transition region. Calculating energy profiles along the reaction coordinate, without reoptimizing the remaining degrees of freedom, is seldom meaningful because of the strong coupling of the coordinates in the transition-state region.

Table IV shows the steps used to find the transition state for the dissociation and the *tert*-butoxy radical to methyl radical and acetone. The first set of calculations was performed at the unrestricted Hartree–Fock (UHF) level, with the 4-21G basis set. The reaction coordinate $Q$ is the $C_1$–$C_2$ bond (see Figure 3), and $C_s$ symmetry was assumed throughout. In step 1, constrained optimization was carried out at $Q$ = 1.837, 2.037, and 2.237 Å. Convergence was achieved in five to eight cycles. A plot of these adiabatic energies as a function of $Q$ indicated that the point at $Q$ = 2.237 Å is close to the estimated transition state. An unconstrained optimization started from this point (step 2) converged to the saddle point in seven steps. Using the 4-21G UHF geometry as a starting point, the saddle point was redetermined at progressively higher levels of theory, at the 3×3 unrestricted natural orbital—complete active space[42] (UNO-CAS) level with the 4-21G, 6-31G*, and 6-311G** basis sets. The UNO-CAS[42] method is an efficient way to obtain a close approximation to the CAS-SCF[43] wave function and is particularly appropriate for transition states. Table IV includes a few important, geometry parameters; it is interesting to observe the shortening of the C–O bond and the flattening of the acetone moiety as the methyl group is leaving.

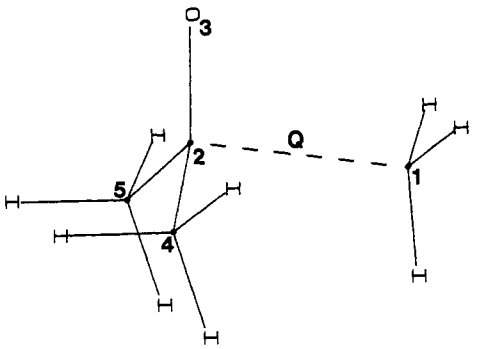


Figure 3. The dissociation of *tert*-butoxy radical into acetone and methyl radical (Table IV).

(41) Lu, D. H.; Zhao, M.; Truhlar, D. G. *J. Comput. Chem.* **1991**, *12*, 376.

(42) Bofill, J. M.; Pulay, P. *J. Chem. Phys.* **1989**, *90*, 3637.

(43) (a) Roos, B. O.; Taylor, P. R.; Siegbahn, P. E. M. *Chem. Phys.* **1980**, *48*, 157. (b) Ruedenberg, K.; Sundberg, K. R. In *Quantum Science*; Calais, J.-L., Goscinski, O., Linderberg, J., Ohrn, Y., Eds.; Plenum: New York, 1976.

## VII. Optimization Using Redundant Coordinates

In some cases of complex molecular topology, it is difficult to avoid redundant coordinates, and our program in its present form generates more internal coordinates than required. The advantage of redundant coordinates is that the force field is often more diagonal in a redundant set; this has been well-known to spectrocopists and was recommended by Schlegel to generate Hessians for the **Z** matrix coordinates.[24] We have recently succeeded in generalizing the geometry optimization procedure to the case of redundant coordinates. We believe that our formulation, which will be described in detail elsewhere,[18] has both practical and theoretical advantages over the transformation method of Schlegel,[24] although it is based on the same principle.

Two examples are shown at the end of Table II. As in all cases discussed in the previous sections, the Hessian **F** was the diagonal guess given by the INTC subroutine. In the present case, however, this refers to a redundant coordinate system, so that the true **F**, in a nonredundant set, is not diagonal. In the first example, that of norbornane (**2f**), the redundant coordinates (referred to as set B) are based on a scheme that uses ring coordinates for the six-membered ring only, treating the bridge as a chain. This results in 57 coordinates instead of $3N - 6 = 51$. With set B convergence is achieved in five steps. This is faster than with set A (section V) which needed eight steps.

The second example in Table II is porphine, $C_{20}N_4H_{14}$ (**2g**), a large and biologically important system. The INTC program generates a redundant set of coordinates which contain the five-membered ring coordinates (Figure 2) but does not exclude the six redundancies arising from closing the macrocycle. Convergence is achieved in eight steps, which is quite good for such a large system, even with the $C_{2v}$ symmetry which restricts the number of variables to 37. We used simple RHF theory here, but a correct description, particularly the assessment of the barrier at $D_{2h}$ symmetry, requires the use of a multiconfigurational wave function; these calculations are currently in progress.

## VIII. Empirical Correction of Bond Lengths by Offset Forces

Hartree–Fock theory, although reasonably accurate for most organic systems, still falls short of the accuracy desired. In particular, with double-$\zeta$ or better basis sets, bond lengths are accurate only to a few hundredths of an angstrom.[44] According to a detailed analysis by Hehre et al.,[34] bond lengths between heavy (non-hydrogen) atoms have mean absolute errors between 0.015 and 0.035 Å, depending on the type of bond and the basis set used. To obtain better results, one has to resort either to higher levels of theory, or to empirical corrections. Correction of bond lengths is particularly important for the accurate calculation of vibrational frequencies. Due to strong anharmonicity, calculated harmonic stretching force constants are very sensitive to errors in the bond lengths;[5] a simple estimate based on the Morse potential states that a difference of only 0.016 Å in the bond length causes a change of 10% in the stretching force constant.[45]

The accuracy of calculated bond lengths can be improved significantly empirically because the errors are quite systematic. Such corrections were first introduced by Blom and Altona;[6] they were widely used in the MOCED (molecular orbital constrained electron diffraction) work of Schäfer[7] and in our vibrational studies.[46]

We suggest here a scheme which is close to the above, but is more satisfactory theoretically. Rather than correcting the bond lengths after the optimization, we apply "offset forces" along the corresponding bond stretching coordinates throughout the optimization. This has the advantage the the *empirically modified potential surface* is well-defined; it is the sum of the ab initio energy and a linear function in the bond stretchings. Of course, we assume here that the stretching coordinates are uniquely defined. A linear correction can be justified by the empirical (and little appreciated) fact that near equilibrium the correlation energy is approximately a linear function of the bond distances.[45] The present scheme removes the uncertainty[2] which plagues force constants and harmonic frequencies calculated at nonequilibrium geometries; the second derivatives of the corrected potential surface are as well-defined as those of the original ab initio surface.

Table V. Offset Forces Used for the Empirical Correction of Hartree–Fock Geometries[a]

| bond | range[b] (Å) | offset force 4-21G(*) | offset force 6-31G* |
|---|---|---|---|
| C—H | | +0.06 | +0.04 |
| N—H | | +0.02 | +0.07 |
| O—H | | −0.02 | +0.09 |
| C—C | >1.42 | −0.05 | 0.00 |
| C÷C(arom.) | 1.42–1.38 | +0.10 | +0.09 |
| C=C | 1.38–1.28 | +0.23 | +0.19 |
| C≡C | <1.28 | +0.35 | +0.34 |
| C—N | >1.35 | +0.02 | +0.10 |
| C÷N(arom) | 1.35–1.30 | +0.10 | +0.16 |
| C=N | 1.30–1.20 | +0.26 | +0.28 |
| C≡N | <1.20 | +0.52 | +0.47 |
| C—O | >1.30 | +0.02 | +0.14 |
| C=O | <1.30 | +0.20 | +0.32 |
| C—F | | +0.09 | +0.13 |
| C—Cl | | −0.10 | −0.03 |
| (C—S)[c] | (>1.65) | (−0.05) | |
| (N=N)[c] | (1.25–1.15) | (+0.4) | (+0.4) |
| N=O[d] | 1.25–1.20[d] | +0.36 | +0.40 |

[a] In aJ Å$^{-1}$. [b] The range of bond length that defines the bond type. [c] Preliminary, tentative results. [d] Only the narrow range of organic nitro groups tested yet.

It is difficult to improve bond angles empirically, and their error, often a degree or less for rigid molecules, is acceptable in many cases. The best strategy to improve bond angles is to use polarized basis sets, particularly on atoms with lone pairs. Accordingly, we use corrections for bond lengths only.

Table V contains our recommended offset forces for some of the most important bonds in organic chemistry. A preliminary version of this table was published earlier.[28] Because of its modest computing cost, we plan to use the 4-21G(*) basis: in the ideal case, after correction the results should be independent of the basis. Still, in some cases the 6-31G* basis set may be necessary, and the offset forces were determined for both basis sets. The procedure was as follows. For each bond type a few basic molecules, for which the experimental geometries seemed reliable, were selected as references. From a gradient calculation in the experimental geometry, the offset force is the negative of the ab initio force along the bond. These were averaged for the group of reference molecules. Note that separate offset forces are used for single, aromatic, double, and triple bonds between the same atoms. This is at variance with our earlier procedure[5] where a formula was used to give the correction (of bond length) as a function of the uncorrected bond length. The present scheme is simpler. It has, however, the disadvantage that it introduces discontinuities, and cannot be used, for example, in bond breaking cases; in such cases, of course, the simple Hartree–Fock wave function to which our corrections refer is inadequate anyway. A more important but fortunately infrequent problem is the prediction of bond lengths which are intermediate, e.g., between the C—C and C=C bonds. We tried to chose the ranges for different bond types so that there are few bond lengths close to them. This difficulty would be eliminated by using an interpolation formula like that in ref 5 but at the cost of additional complexity in the geometry optimization.

We have tested the suggested method on more than 60 organic molecules of various types, with the number of distinct bonds exceeding 200. Due to space limitations, only some illustrative examples are shown in Table VI. (The complete tabulation of results will be published separately.) It is thus not possible to discuss individual molecules. Instead, to show the overall performance of empirical corrections, a statistical analysis is given

(44) Pople, J. A. In *Applications of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; p 1.
(45) Pulay, P.; Lee, J. G.; Boggs, J. E. *J. Chem. Phys.* **1983**, *79*, 3382.
(46) (a) Corrections for basic bond types were suggested in ref 5. (b) For a survey, see also ref 8a. (c) For some recent applications, see also refs 8c and 8d.

**Table VI.** Sample Examples of Calculated Bond Lengths Obtained by Using Offset Forces as Empirical Corrections[a]

| | | without offset forces | | with offset forces | | |
|---|---|---|---|---|---|---|
| bond | molecule | 4-21G(*) | 6-31G* | 4-21G(*) | 6-31G* | exptl[b] |
| C—C | propane | 1.541 | 1.528 | 1.528 | 1.528 | 1.526 |
| | propene | 1.511 | 1.503 | 1.498 | 1.501 | 1.501 |
| | butadiene | 1.470 | 1.468 | 1.457 | 1.465 | 1.465 |
| | but-1-yne-3-one | 1.435 | 1.439 | 1.424 | 1.437 | 1.434 |
| | hexatriene | 1.465 | 1.463 | 1.452 | 1.460 | 1.458 |
| | acetaldehyde | 1.519 | 1.504 | 1.504 | 1.509 | 1.501 |
| | acetonitrile | 1.466 | 1.468 | 1.455 | 1.467 | 1.458 |
| | glyoxal | 1.530 | 1.517 | 1.513 | 1.511 | 1.527 |
| | cyclopropene | 1.524 | 1.495 | 1.512 | 1.495 | 1.509 |
| | benzaldehyde[c] | 1.488 | 1.483 | 1.474 | 1.478 | 1.476 |
| | phenylacetylene | 1.438 | 1.443 | 1.445 | 1.441 | 1.448 |
| | *p*-benzoquinone | 1.495 | 1.489 | 1.481 | 1.485 | 1.481 |
| C+C (arom.) | benzene | 1.384 | 1.386 | 1.396 | 1.396 | 1.396 |
| | 1,3,5-trichlorobenzene | 1.379 | 1.382 | 1.392 | 1.393 | 1.392 |
| | pyrazine | 1.383 | 1.386 | 1.394 | 1.395 | 1.403 |
| | triphenylmethane[d] | 1.385 | | 1.397 | | 1.403 |
| C=C | propene | 1.314 | 1.318 | 1.336 | 1.336 | 1.336 |
| | butadiene | 1.319 | 1.323 | 1.341 | 1.341 | 1.345 |
| | but-1-yne-3-ene | 1.319 | 1.322 | 1.341 | 1.340 | 1.344 |
| | hexatriene | | | | | |
| | C(1)-C(2) | 1.320 | 1.324 | 1.343 | 1.342 | 1.337 |
| | C(3)-C(4) | 1.325 | 1.329 | 1.350 | 1.349 | 1.368 |
| | allene | 1.291 | 1.296 | 1.311 | 1.312 | 1.308 |
| | ketene | 1.302 | 1.306 | 1.323 | 1.322 | 1.314 |
| | cyclopropene | 1.282 | 1.276 | 1.301 | 1.291 | 1.296 |
| | cyclopentadiene | 1.327 | 1.329 | 1.353 | 1.348 | 1.345 |
| | acrolein | 1.316 | 1.321 | 1.338 | 1.339 | 1.345 |
| | *p*-benzoquinone | 1.318 | 1.323 | 1.341 | 1.342 | 1.344 |
| C≡C | but-1-yne-3-ene | 1.188 | 1.186 | 1.206 | 1.206 | 1.215 |
| | cyanoacetylene | 1.185 | 1.185 | 1.204 | 1.203 | 1.205 |
| | phenylacetylene | 1.188 | 1.189 | 1.206 | 1.206 | 1.208 |
| C—N | methylamine | 1.475 | 1.453 | 1.478 | 1.472 | 1.474 |
| | nitromethane | 1.494 | 1.479 | 1.493 | 1.495 | 1.490 |
| | nitrobenzene | 1.467 | 1.459 | 1.461 | 1.469 | 1.478 |
| C+N (arom.) | pyridine | 1.328 | 1.321 | 1.338 | 1.337 | 1.338 |
| | pyrazine | 1.326 | 1.319 | 1.336 | 1.335 | 1.339 |
| C—O | dimethylether | 1.414 | 1.392 | 1.416 | 1.415 | 1.415 |
| | phenol | 1.366 | 1.353 | 1.368 | 1.372 | 1.374 |
| | *o*-chlorophenol | 1.357 | 1.345 | 1.359 | 1.364 | 1.37 |
| C=O | acetaldehyde | 1.193 | 1.188 | 1.206 | 1.209 | 1.215 |
| | benzoic acid[e] | 1.188 | 1.184 | 1.202 | 1.203 | (1.24) |
| | salicylic acid[e] | 1.208 | 1.202 | 1.223 | 1.225 | (1.241) |
| | *p*-benzoquinone | 1.199 | 1.194 | 1.214 | 1.216 | 1.225 |

[a] All values in angstroms. For the offset forces, see Table V. [b] Unless otherwise indicated, all experimental data are taken from the Landolt-Börnstein collection, ref 47. [c] Experimental values from NMR results in liquid crystal solvent: Diehl, P.; Jokisaari, J.; Amrein, J. *Org. Magn. Reson.* **1980**, *13*, 451. [d] Average value is given, because only this is available experimentally; in the calculation, the individual CC bond lengths in a ring show a variation of up to 0.01 Å. The 6-31G* calculation was not done because it would exhaust our disk capacity of ~1 GB. [e] The experimental values in parentheses come from X-ray studies of the hydrogen-bonded dimers; benzoic acid: Sim, G. A.; Robertson, J. M.; Goodwin, T. H. *Acta Crystallogr.* **1955**, *8*, 157. Salicyclic Acid: Cochran, W. *Acta Crystallogr.* **1953**, *6*, 260.

in Table VII. This is based on 129 bond lengths, those for which experimental data on the free molecule are available (taken from ref 47). One factor limiting the comparison is the uncertainty of the experimental values. These arise partly from measuring errors but mostly from vibrational effects. Even microwave substitution ($r_s$) structures, normally assumed to be close to the equilibrium values, may occasionally exhibit large errors.[48] In general, for distances between non-hydrogen atoms, the mean error in the experimental bond lengths is probably near or slightly below 0.01 Å. In light of this, the corrections work very satisfactorily: as seen in the first row of Table VII, the mean absolute error goes down from 0.014 to 0.005 Å. The number of deviations exceeding a given limit is also shown. At the 0.02-Å level, there is no discrepancy for the 4-21G(*) basis and only one for the 6-31G* basis. The latter discrepancy was found in 1,2-cyclobutanedione, where the C–C bond distance between the two carbonyl groups comes out too short: 1.551 Å as compared to the experimental value of 1.574 Å. (Surprisingly, the 4-21(*) result is 1.577 Å, in good agreement with experiment.) In any case, this one single discrepancy should be compared to the more than 30 discrepancies without corrections. Using a stricter criterion, there are still only five cases of deviations larger than 0.015 Å. Because of the experimental uncertainty in the bond lengths, the last row of Table VII is hardly significant and was added only to complete the statistics.

The last column of Table VII gives information about the internal consistency of the theoretical results: while two different basis sets give, of course, considerable differences in the calculated bond lengths, these differences should be largely eliminated by the empirical corrections. This requirement is fairly but not

(47) *Landolt-Börnstein, Zahlenwerte und Funktionen aus Naturwissenschaften und Technik (Numerical Data and Functional Relationships in Science and Technology)*; Neue Serie; Madelung, O., Ed.; Group II, Vol. 15: Structure Data of Free Polyatomic Molecules; Callomon, J. H., Hirota, E., Iijima, T.; Kuchitsu, K., Lafferty, W. J., Eds.; Group II, Vol. 7: Structure Data of Free Polyatomic Molecules, Callomon, J. H., Hirota, E., Kuchitsu, K., Lafferty, W. J., Maki, A. G., Pote, S. S., Eds.; Springer-Verlag: Berlin-Heidelberg, 1987.

(48) Boggs, J. E.; Altman, M.; Cordell, F. R.; Dai, Y. *THEOCHEM* **1983**, *11*, 373.

Table VII. Statistical Analysis of the Results on Bond Lengths[a]

| property | theoret vs exptl: without offset forces 4-21G(*) | theoret vs exptl: without offset forces 6-31G* | theoret vs exptl: with offset forces 4-21G(*) | theoret vs exptl: with offset forces 6-31G* | theoret vs theoret[b] 6-31G* − 4-21G(*) |
|---|---|---|---|---|---|
| mean absolute error | 0.014 | 0.014 | 0.005 | 0.005 | 0.003 |
| maximum deviation | 0.043 | 0.039 | 0.018 | 0.023 | 0.026 |
| number of deviations larger than | | | | | |
| Δ = 0.020 | 31 | 35 | 0 | 1 | 1 |
| Δ = 0.015 | 49 | 55 | 5 | 5 | 3 |
| Δ = 0.010 | 88 | 76 | 17 | 14 | 7 |

[a] Bond lengths in angstroms. Based on 129 data points of which some examples are listed in Table VI. See also the text. [b] Using the offset forces corrections.

completely satisfied: while the mean deviation is only 0.003 Å, there are seven deviations exceeding 0.01 Å, with three of them above 0.015 Å and the maximum deviation is 0.026 Å. (The latter is the C–C bond in cyclobutanedione discussed above.)

Although the corrected bond distances show excellent overall agreement with experiment, it is evident that a simple empirical correction has limitations, mainly for strongly strained systems and for conjugated systems where nondynamical correlation effects are present. This is clearly indicated by the fact that, beyond cyclobutanedione, the rest of the larger deviations (those exceeding 0.015 Å) were found in the following molecules: glyoxal, hexatriene, cyclopropene, aziridine, and nitrobenzene. It should also be noted that virtually all the bonds investigated were of the type where one of the atoms is carbon; the method may work slightly less well for some less common bonds. The latter are, fortunately, less important in organic chemistry. Perhaps the weakest point of our procedure is the discontinuity in the corrections discussed above. For example, when going from a single C—C bond to a C=C double bond there is a sudden change in the offset force used as correction (Table V). In most cases of well isolated bonds this presents no problem. However, we realize that there is some uncertainty, especially in conjugated $\pi$-systems. In the present study we calculated these offset forces from butadiene to octatetrene where the bonds can still be easily classified as single or double bonds and the empirical correction works satisfactorily. In more strongly correlated systems a uniform correction, like in aromatics, may work better. Ultimately, however, one may be forced to use higher levels of theory. We are experimenting with the MCSCF type UNO-CAS[42] method.

In contrast to previous schemes, the present procedure has a new feature that should be kept in mind: an offset force along any given bond affects all other geometrical parameters. Since couplings between stretchings and bendings are quite significant, incorrect bond distances lead to further errors in bond angles. Thus, we expect that the use of offset forces to improve bond lengths will lead to improvements in the angles too. This should be more significant for the 6-31G* basis, which reproduces the bond angles much better than the 4-21G(*) basis. We have investigated this on several bond angles, and a compilation of results is available upon request. The changes caused by the offset forces in the angles are of the order of a few tenths of a degree. The largest change was found for the C–O–H angle in methanol, where the 6-31G* value changed from 109.5° to 108.8° (the experimental value is 108.0°[47]). The basic conclusion is that the changes in angles are not very significant but seem to point in the right direction.

## IX. Conclusions

We have demonstrated by numerous examples that an appropriately defined system of internal coordinates, which we call natural coordinates, can greatly accelerate the convergence of geometry optimizations. The essence of this method is that by using natural coordinates structural information is built into the procedure and couplings, both harmonic and higher order, are reduced. The time-consuming construction of the internal coordinates has been automated and is included in our program system TX90. By interfacing the latter to PCMODEL, a commercial molecular graphics and force field program, the generation of the input for the ab initio program is greatly simplified. Convergence of the geometry for organic molecules is typically achieved in 8–15 steps, even for systems with over 100 degrees of freedom, using a simple diagonal guess of the force field and the GDIIS optimization technique. Because higher order couplings are small in natural coordinates, this system is better than Cartesian coordinates even if a good initial Hessian is available. We have compared the efficiency of geometry optimization in natural internal coordinates with that in Cartesian coordinates and found significant improvement in the rate of convergence, particularly in molecules with soft degrees of freedom.

Although our natural coordinates are nonredundant in most cases, in complex polycyclic systems redundant coordinates are difficult to avoid. We have demonstrated that, contrary to the accepted view, geometry optimization can easily be generalized to handle redundant coordinates.

To increase the accuracy of ab initio geometries, we have introduced empirical corrections in form of 'offset forces' along bond lengths. We have compared 130 experimental bond lengths with the corresponding Hartree–Fock values obtained using two basis sets, 4-21G(*) and 6-31G*. Although empirical correction schemes have obvious limitations, the offset forces reduce the average error in normal bonding situations from 0.014 to 0.005 Å for both basis sets.

Both the efficient geometry optimization method developed here and the empirical correction of bond lengths represent the first step toward a major project of large-scale vibrational frequency calculations started in this laboratory recently.[28] The final goal of this project is to build a data base of accurate geometries and force constants.

**Acknowledgment.** This project has been supported by the National Science Foundation under Grant No. CHE-8814143. We are grateful to IBM Co. for the donation of an RS-6000 workstation to our Department and the loan of another.