Some Practical Suggestions for Optimizing Geometries and Locating Transition States

H. Bernhard Schlegel
Department of Chemistry
Wayne State University
Detroit, Michigan, 48202
USA

ABSTRACT The optimization of equilibrium geometries and transition states by molecular orbital methods is discussed from a practical point of view. Most of the efficient geometry optimization methods rely on analytical energy gradients and quasi-Newton algorithms. For any optimization method, there are three areas of input that directly affect the behavior of the optimization: (a) the choice of internal coordinates, (b) the starting geometry and (c) the initial estimate of the Hessian. A number of topics related to these three areas are discussed with the aim of improving the performance of optimizations; these include symmetry, dummy atoms, avoiding coordinate redundancy, overcoming strong coupling among coordinates, conversion between coordinate systems, testing stationary points and what to do when optimizations fail.

1. Introduction

Equilibrium geometries can be calculated routinely, reliably and accurately by ab initio molecular orbital methods [1]. In principle, transition states can be calculated equally well; though, in practice, transition structures require a little more skill to optimize than equilibrium structures. The importance of geometry optimization is supported by the fact that most molecular orbital calculations appearing in the chemical literature in recent years involve geometry optimization to some degree [2,3]. In this Chapter, some of the practical aspects of geometry optimization are considered.   The discussions are based on the GAUSSIAN series of programs [4] (the optimization tools available in the GAUSSIAN system are listed in the Appendix), but the concepts and suggestions can be applied directly to any semi-empirical or ab initio MO program that uses internal coordinates for geometry optimization. Most molecular mechanics or empirical force field programs carry out the optimization in Cartesian coordinates, and hence are outside the scope of this Chapter.

Geometry optimization has become routine primarily because of the availability of efficient programs to calculate analytical energy gradients (for recent reviews see [5-8]). Analytical gradient based geometry optimizations are almost an order of magnitude faster than optimization methods that use only the energy. Almost all user-friendly molecular orbital programs have analytical gradients at the Hartree-Fock (HF) level; many have analytical gradients for the second order Møller-Plesset perturbation theory (MP2). Some

33

programs can also compute analytical gradients at the MP3 [9], MP4 [10], configuration interaction [11], coupled clusters [12] and MCSCF [13] levels. Many semi-empirical programs also have analytical gradients. In addition to first derivatives of the energy, some calculations also require second derivatives, e.g. vibrational frequencies. Second derivatives can be calculated by numerical differentiation of analytical first derivatives or, more efficiently, by analytical second differentiation of the energy [14]. A number of programs can calculate analytical second derivatives at the Hartree-Fock level; a few can calculate analytical second derivatives at the MP2 [15], CI [16] and MCSCF [17] levels. Third derivatives can also been calculated analytically at the Hartree-Fock [18] and two configuration SCF levels [19]. Additional details of the theory of analytical derivatives can be found in various articles and reviews [5-8, 20-22] and references cited therein..

Details of the various algorithms used for geometry optimization and transition structure searching can be found in recent reviews [23-25], and will not be covered in the present Chapter. From a numerical analysis point of view, geometry optimization is just a problem in unconstrained minimization [26-28]. The books by Scales [26], and Fletcher [27] are quite readable and discuss a wide variety of algorithms for unconstrained minimization, with special emphasis on methods employing gradients. Locating a transition structure is somewhat more difficult than finding a minimum. A transition structure is a maximum in one and only one direction on the potential energy, and is a minimum in all other directions (i.e. a first order saddle point or col). During the course of a transition structure search, the algorithm must choose the best direction along which the energy is maximized, as well as carrying out the maximization in that direction and the minimization in all other directions. Compared to unconstrained minimizations, the numerical analysis literature on saddle point optimizations is much less extensive ([26-28] and references cited). From a chemical point of view, a number of methods for finding transition states have been proposed; details of some of these algorithms can be found in recent reviews [23,24] and references therein.

Most programs provide a brief write-up of how to use their particular optimization code. A useful outline for geometry optimization can also be found in "A Handbook of Computational Chemistry" [29]. However, there does not seem to be a practical guide on the details of geometry optimizations and transitions structure searches. The purpose of this Chapter is to provide a few hints to help set up optimizations so that they will work better (Sections 4-12), and to provide some suggestions of what to try when optimizations go wrong (Section 13).

2. Symmetry and Stationary Points

Symmetry can be quite helpful in speeding up optimizations of minima and saddle points, but can also create difficulties by constraining the search to a subsection of the energy surface. If a molecule has any symmetry, it should be used to reduce the number of coordinates that must be optimized. This can be beneficial even if the molecule has only C_s or C_2 symmetry. Taking advantage of symmetry may also fix some flexible coordinates, such as internal rotations, that would otherwise slow down the optimization. In favorable circumstances, symmetry can even be used to turn a transition structure optimization into a minimization (see below).

Symmetry can also cause problems. By symmetry, the gradients must belong to the totally symmetric representation of the point group of the molecule. This means that a gradient based optimization method will not change the symmetry of the molecule during the course of an optimization (provided the internal coordinates properly reflect the symmetry of the molecule). Hence, a molecule will not distort to a lower symmetry during

an optimization, even if the lower symmetry structure is lower in energy. Therefore, once the structure has been optimized, it must be tested to ensure that displacements to lower symmetries do not lower the energy (see below - 12. Testing Stationary Points). By contrast, there are no restriction on optimizations going to higher symmetry; however such optimizations may be slow because of strong coupling between symmetry equivalent coordinates. Under such circumstances, it may be unclear if the optimization will converge to a slightly distorted structure or if the optimization is actually proceeding to a higher symmetry structure. If a higher symmetry structure is suspected, it is often more efficient to optimize the higher symmetry structure directly and test it for stability with respect to distortion to lower symmetry (Section 12).

Some transition structure optimizations can be turned into minimizations by symmetry. Stanton and McIver [30] have discussed a number of symmetry restrictions on transitions states; the ones directly relevant to transition structure optimization can be summarized as follows:

(a) a transition vector cannot belong to a degenerate representation (otherwise there would be at least 2 equivalent eigenvectors of the Hessian with negative eigenvalues, and the structure is at least a second order saddle rather than a first order saddle point),

(b) the transition vector must be symmetric for all symmetry operations of the transition state that also leave the reactants and products unchanged,

(c) the transition vector must be antisymmetric for any of the symmetry operations of the transition state that interconvert the reactants and products.

For most reactions, only (a) and (b) can be used to simplify the transition structure optimization. However, in some reactions, such as racemizations, degenerate isomerizations, identity exchanges, etc., reactants and products can be interchanged by a symmetry operation of the transition state (e.g. a C_2 axis for the 1,3 antara hydrogen shift $CH_3CH=CH_2 \rightleftharpoons CH_2=CHCH_3$; a σ plane for the identity S_N2 reaction $X^- + CH_3X \rightleftharpoons XCH_3 + X^-$). The effect of (c) for these types of reactions is to constrain the transition state to be at the midpoint of a symmetric reaction path connecting reactants and products. Since the reaction path is the direction along which a maximum must be found and the position of this maximum given by symmetry; what remains to be done in the transition structure optimization is to minimize with respect to all of the remaining (totally symmetric) displacements in the transition state. Thus, for these special cases, the transition structure optimization is reduced to a simple minimization. The final transition structure should still be tested to ensure that it is a valid transition state (i.e. with one and only one negative eigenvalue in the full Hessian, Section 12).

3. The Basic Optimization Step

Most of the algorithms for geometry optimization using gradients rely on a quadratic expansion of the energy surface [26-28]. In terms of the coordinates, $\vec{x}_0$, the calculated energy, E_0, the calculated gradient, $\vec{g}_0$, and an approximate second derivative matrix or Hessian, $\underline{H}$, the energy and gradient are written as:

$$E = E_0 + \vec{g}^T (\vec{x} - \vec{x}_0) + \frac{1}{2} (\vec{x} - \vec{x}_0)^T \underline{H} (\vec{x} - \vec{x}_0) \tag{1}$$

$$\vec{g} = \vec{g}_0 + \underline{H} (\vec{x} - \vec{x}_0) \tag{2}$$

At the optimized geometry, the gradient is zero; therefore, the next estimate of the optimum geometry is found by solving eq (2) for $\vec{g} = 0$, i.e. a Newton-Raphson step:

$$\vec{x} = \vec{x}_0 - \underline{H}^{-1} \vec{g}_0 \qquad\qquad (3)$$

Almost all of the algorithms have these steps in common; thus, almost all optimization methods need a starting geometry and an initial estimate of the Hessian. Much of this Chapter will deal with the choice of internal coordinate system for an optimization, the starting geometry and the initial estimate of the Hessian.

The various optimization algorithms differ in the way the estimated Hessian is updated at each step (e.g. DFP, MS, BFGS, etc.), how the solution of eq (3) is constrained (e.g. reduction of steps that are larger than the trust radius) and how the one dimensional optimization is carried out along the direction predicted by eq (3) (e.g. accurate, approximate or not at all). The details can be found in a various books and review articles [23-28]. Given the same starting conditions, most of the recent gradient algorithms perform similarly. The BFGS method with a very approximate line search seems to be quite efficient for geometry minimization [31]. Aside from GAUSSIAN (see Appendix), most molecular orbital programs have only a limited selection of optimization algorithms and one must work within the framework of the available code. Thus, success or failure in an optimization using a particular program will depend significantly on the starting conditions of the optimization. The 3 most important areas are (a) choice of the internal coordinates (Sections 4-7), (b) the starting geometry (Sections 8-10) and (c) the initial estimate of the Hessian (Section 11).

4. Choice of Internal Coordinates

Although a good geometry optimization program should converge regardless of the coordinate system, most practical optimization problems converge much faster when the coordinate system is constructed with some care. Strong coupling between coordinates invariably causes difficulties for optimizations. The coupling between stiff coordinates (stretch, bend etc.) and loose coordinates (e.g. internal rotations and inversions with low barriers) can be especially troublesome. Cyclic molecules have inherently strongly coupled internal coordinates, and suffer from additional difficulties because of redundant coordinates. Transition structures are sometimes quite flexible, and coupling between these flexible modes and the transition vector may lead to additional problems. Loosely bound clusters are a third category of potentially troublesome optimizations, because large changes in geometry may occur with small changes in the energy.

Internal coordinates for the GAUSSIAN system of programs are defined using the Z-matrix notation [4]; other programs use similar systems to define internal coordinates (see [29]) and the appropriate user manual should be consulted for details. To facilitate the discussion of internal coordinate systems, an example of a Z-matrix input for methanol is given below. For the first atom, C, only the name of the atom is required; for atom 2, the name of the atom (O), the number of the atom to which it is bonded (1) and the distance (1.48 Å) are required. The third line indicates that atom 3 is an H, bonded to atom 2 at a distance of 0.96 Å and makes an angle with atom 1 of 105.0° (i.e. <321). Atom 4 is an H, bonded to atom 1 at a distance of 1.08 Å, makes a valence angle with 2 of 109.5° (<412) and a dihedral angle with 3 of 180° (i.e. <4123, the angle of rotation between 4 and 3 about the axis formed by atoms 1 and 2). Subsequent atoms are defined in a similar way in terms of a distance, valence angle and a dihedral angle to previously defined atoms. In some programs (e.g. GAUSSIAN), a second valence angle can be used instead of the dihedral angle (see Example 7). The appropriate user manual should be consulted for the details of specifying internal coordinates for a particular MO program.

Example 1. Z-matrix for methanol

```
C
O   1  1.48
H   2  0.96   1  105.0
H   1  1.08   2  109.5   3   180.
H   1  1.08   2  109.5   4   120.
H   1  1.08   2  109.5   4  -120.
```
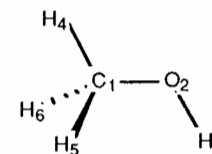

In addition to real atoms, most programs allow dummy atoms to be used in the description of the geometry. Dummy atoms have no charge and carry no basis functions; they are used solely to help define the geometry so that a more convenient set of distances and angles can be used. Dummy atoms are identified by a particular atomic symbol or atomic number (X, - or -1 in GAUSSIAN, see Example 3) and are specified in the same manner as regular atoms. Some examples that are discussed below include linear molecules (to avoid valence angles of 180°), molecules undergoing inversion (so that the entire path from reactants to products can be followed with the same Z-matrix), cyclic molecules (to uncouple coordinates that are too strongly coupled) and transition states (to help separate the transition vector from the remaining coordinates).

To permit geometry optimization in GAUSSIAN, the values for distances and angles to be optimized are replaced by variable names. Initial values are supplied for these parameters and the optimization code varies these parameters in the search for the stationary point. There are numerous other features in the GAUSSIAN Z-matrix input [4], but the limited set illustrated here is sufficient for the examples discussed below.

Example 2. Symbolic Z-matrix for methanol (HF/3-21G optimized values)

```
C
O   1  RCO
H   2  ROH    1  ACOH
H   1  RCH1   2  AOCH1  3   180.
H   1  RCH2   2  AOCH2  4   DHOCH2
H   1  RCH2   2  AOCH2  4  -DHOCH2
```
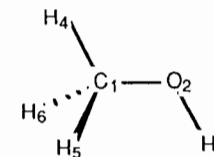

RCO=1.440, ROH=0.966, RCH1=1.079, RCH2=1.085, ACOH=110.4, AOCH1=106.3, AOCH2=112.3, DHOCH2=118.5

Most programs impose some restriction on the value of distances and angles used to construct the geometry. Distances are usually required to be positive, valence angle must be greater than 0° but less than 180° and dihedral angles typically have a range of -180° to +180° or -360° to +360°. Other restrictions may be imposed by the symmetry of the molecule (e.g. if an angle is tetrahedral by symmetry, 109.4712° ··· should be used and not 109.5°). Some care must be taken that the limits on the bond lengths and angles are not exceeded during the course of an optimization. For example, a molecule with 3 atoms nearly linear such as HOCN (or any molecule with a fragment that can approach linearity during an optimization) can be specified with a dummy atom and thus avoiding the restrictions on the valence angle.

Example 3. Symbolic Z-matrix for cyanic acid (HF/3-21G)

```
C
N  1  RCN
X  1  1.0    2  90.
O  1  RCO    3  AXCO  2  180.
H  4  ROH    1  ACOH  3  180.

RCN=1.140, RCO=1.308, ROH=0.970,
AXCO=88.7, ACOH=114.2
```
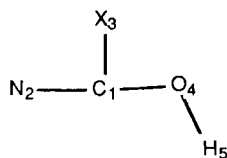

5. Internal Coordinates, Symmetry and Dummy Atoms

Some useful guidelines for constructing internal coordinate systems can be developed for molecules with some degree of symmetry [32a]. Specifically, symmetry can be quite helpful in setting up dummy atoms and in defining the connectivity for the internal coordinates. For example, cyclic molecules can lead to very strongly coupled coordinate systems, but if there is sufficient symmetry, a well behaved, relatively uncoupled coordinate system can be constructed. Even if a molecule possesses very little symmetry, a suitable set of internal coordinates may be obtained by taking a higher symmetry analogue of the molecule and systematically reducing the symmetry.

For molecules with more than 3 or 4 atoms and with some symmetry, it may be best to define the atoms on the highest symmetry elements first:

(a) If there is an atom at the center of inversion, the intersection of 2 or more rotational axes, or the intersection of an axis and a perpendicular plane, specify that atom first (e.g. S in SF_6). If there is no atom at the center of symmetry, put a dummy atom there (e.g. the middle of the ring in cyclopropane, C_3H_6).

(b) If there are axes of rotation, specify the atoms on the highest order axis first (e.g. C and F on the C_3 axis in CH_3F). If there is only 1 atom on the axis, add a dummy atom on the axis (e.g. in the direction of the lone pair NH_3, or on the bisector of <HCH and <FCF in CH_2F_2). Some cases, such as rings, may require 2 dummy atoms to define the axis (e.g. C_3H_6).

(c) If there is only a plane of symmetry and no other elements of symmetry, specify at least 2 and preferably 3 atoms in the plane first (e.g. N, O and H in H_2NOH). If there are less than 2 or 3 atoms in the plane, add enough dummy atoms to define the plane so that the remaining atoms can be specified relative to the plane.

In specifying the other atoms in the molecule, it is best to group them into symmetry equivalent sets (e.g. the 3 C's in cyclopropane form one set and the 6 H's form another set). For each atom in a symmetry equivalent set:

(d) Define the bond lengths and angles in symmetry equivalent ways (e.g. in CH_3F, each H is bonded to C and makes an angle with F).

(e) Use the same variable name for equivalent bond lengths, valence angles and dihedral angles (caution, while valence angles do not change under any symmetry operation, dihedral angles must change sign on reflection or improper rotation).

Example 4. Symbolic Z-matrix for cyclopropane illustrating the use of dummy atoms and symmetry

```
X
X  1  1.0
C  1  RXC  2  90.
C  1  RXC  2  90.  3  120.
C  1  RXC  2  90.  3  240.
H  3  RCH  1  AXCH  2  0.
H  3  RCH  1  AXCH  2  180.
H  4  RCH  1  AXCH  2  0.
H  4  RCH  1  AXCH  2  180.
H  5  RCH  1  AXCH  2  0.
H  5  RCH  1  AXCH  2  180.
```


RXC=0.8735, RCH=1.072, AXCH=122.6
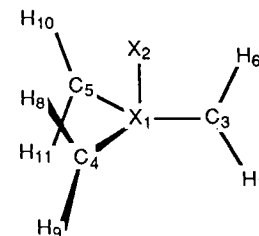
## 6. Full Optimizations and the Number of Internal Coordinates

Whenever possible, a full optimization should be carried out. With the current gradient based optimization methods, most full optimizations are not appreciably longer than partial optimizations and one has the assurance that subtle features of the energy surface are not masked by artificial geometric constraints. For a molecule without symmetry, there are 3n-6 internal coordinates, where n is the number of atoms and all 3n-6 degrees of freedom must be varied in a full optimization.

A frequent cause of difficulty in optimizations is the specification of too few or too many coordinates. Too few coordinates corresponds to a constraint on the geometry of the molecule and results in a less than complete optimization. Too many coordinates results in a redundancy among the internal coordinates, leading to zero eigenvalues in the Hessian and to very poor behavior during the optimization. If there are no dummy atoms and no symmetry, the Z-matrix input contains 3n-6 unique parameters, all of which must be varied in a full optimization. When dummy atoms are present, some of the Z-matrix parameters are redundant and must be held fixed.

In Example 5, a dummy atom is needed to specify a nearly linear NCO angle. Clearly, changing the distance to the dummy atom, RCX, does not alter the position of the real atoms. Hence RCX is redundant and must not be included in the optimization. A more subtle redundancy exists between the angles about the dummy atom, ANCX and AXCO. A change in either will bend the NCO angle. But if one angle is increased and the other is decreased by the same amount, the NCO angle remains the same. Hence, only one of the angles can be included in the optimization, and the other must remain fixed, as shown in Example 3 (the 2 dihedral angles are also fixed because the molecule is planar).

Example 5. Symbolic Z-matrix for HOCN with errors due to redundant coordinates.

```
C
N  1  RCN
X  1  RCX  2  ANCX
O  1  RCO  3  AXCO  2  180.
H  4  ROH  1  ACOH  3  180.
```
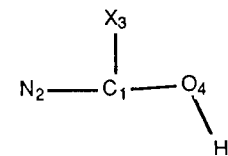
If the molecule has some symmetry, there are fewer than 3n-6 parameters to optimize (if symmetry is to be retained during the optimization). The number of parameters to be optimized can be determined from the symmetries of the normal modes of vibration of the molecule. Only displacements along totally symmetric vibrational modes will retain the symmetry of the molecule; displacement along any of the non-totally symmetric modes will distort the molecule to a lower symmetry. Thus, the number of degrees of freedom that must be included in a full optimization of a molecule within a given symmetry is equal to the number of totally symmetric vibrational modes.

If character tables are not available, an alternative scheme can be constructed to count the number of coordinates required in a full optimization. All the information needed is contained in the framework group notation for the molecule [33]. Each symmetry equivalent set of atoms (dummy atoms excluded) contributes the smallest of the following to the number of degrees of freedom:

(a) 0 if an atom in the set is at the center of inversion, the intersection of two axes of rotation or the intersection of a σ_h plane and an axis,

(b) 1 if an atom in the set is on a proper or improper rotation axis,

(c) 2 if an atom in the set is in a symmetry plane,

(d) 3 if not in any symmetry element.

To account for translational and rotational invariance, the smallest of the following is subtracted from the above sum to yield the number of internal coordinates that must be optimized in a full optimization:

(a) 0 if there is an intersection of two axes of rotation (D_n, D_{nh}, D_{nd} and the cubic groups),

(b) 1 if there is a rotational axis and a symmetry plane (C_{nv}, C_{nh}),

(c) 2 if there is only a rotational axis (C_n, S_n),

(d) 3 if there is only a center of inversion or one symmetry plane (C_i, C_s),

(e) 6 if there is no symmetry (C_1).

This procedure can be illustrated by examining pyramidal trimethylamine, $N(CH_3)_3$, which has C_{3v} symmetry. The N is on the C_3 axis (+1), 3 equivalent C's are in the σ_v planes (+2), 3 equivalent H's are in the σ_v planes (+2), 6 equivalent H's are not on any symmetry element (+3) and finally, subtract 1 for rotation and translation because of the σ_v planes and a C_3 axis. Thus, the total number of coordinates to be optimized is 1+2+2+3-1=7.

## 7. Strong Coupling between Internal Coordinates

Many of the problems encountered in optimizations (see Section 13) can be traced to a poor choice of coordinate system. In general, strong coupling between coordinates degrades the performance of any optimization algorithm. In particular, coupling between stiff modes (e.g. bond stretch, angle bend, etc.) and flexible modes (e.g. torsion about single bonds, inversions with low barriers, interfragment coordinates in loose clusters, etc.) should be kept to a minimum. Similarly in transition states, as few coordinates as possible should be combined to form the transition vector. It is difficult to make more specific statements about good coordinate systems versus bad, but often symmetry and the judicious choice of dummy atoms can be used to improve a coordinate system (Section 5).

As far as possible, natural valence coordinates (bond lengths and angles) should be used to define an internal coordinate system. For acyclic molecules, this is quite easy in the Z-matrix format. The use of symmetry is straight-forward and often dummy atoms are not needed. However, some care must be taken with torsional modes and with nearly planar trigonal centers. Example 6 illustrates the problem of methyl rotation in CH_3SHO. Each of the hydrogens in the methyl group could be defined with a dihedral angle to the SO bond; however, this would require all 3 angles to change by the same amount if the methyl group is rotated in the course of an optimization. Alternatively, a single dihedral angle can be used to specify the rotation of the entire methyl group, thereby decoupling the flexible mode (methyl rotation) from the stiff modes (HCH bend). The same idea can be applied to any group that can rotate.

Example 6. Symbolic Z-matrix for methyl sulphoxide

(a) Methyl rotation strongly coupled.   (b) Methyl rotation decoupled from HCH bend.

```
S                                S
O 1 RSO                          O 1 RSO
H 1 RSH 2 AOSH                   H 1 RSH 2 AOSH
C 1 RSC 2 AOSC 3 DHOSC           C 1 RSC 2 AOSC 3 DHOSC
H 4 RCH1 1 ACH1 2 BCH1           H 4 RCH1 1 ACH1 2 BCH1
H 4 RCH2 1 ACH2 2 BCH2           H 4 RCH2 1 ACH2 5 DCH2
H 4 RCH3 1 ACH3 2 BCH3           H 4 RCH3 1 ACH3 5 DCH3
```
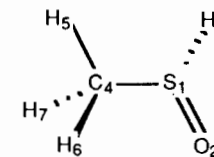
Example 7 shows pyramidal CH_3 that will become planar during the optimization. If 3 valence angles are used to define a nearly planar geometry, then a small change in the angles will cause a large out-of-plane displacement. However, if a dummy atom is placed on the C_3 axis, then the variable BXCH can define the entire inversion process smoothly.

Example 7. Symbolic Z-matrix for out-of-plane bending in CH_3

(a) potential problems   (b) better coordinates

```
C                             C
H 1 RCH                       X 1 1.0
H 1 RCH 2 AHCH                H 1 RCH 2 BXCH
H 1 RCH 2 AHCH 3 AHCH 1       H 1 RCH 2 BXCH 3 120.
                              H 1 RCH 2 BXCH 3 240.
```
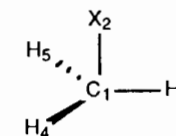
Cyclic molecules are considerably more difficult to specify than acyclic molecules, primarily because the natural valence coordinates have unavoidable redundancies. For example, a planar 5 membered ring has 5 bonds and 5 valence angles for a total of 10 in-plane coordinates; however, there are only 7 degrees of freedom to optimize (C_s symmetry). Thus each valence coordinate is necessarily strongly coupled to the others. Examples 8 and 9 illustrate 2 coordinate systems for each of three model planar rings C_5 (D_{5h}, e.g. the heavy atom skeleton for $C_5H_5^-$), C_4O (C_{2v}, the skeleton for furan) and C_3NO (C_s, the skeleton for isoxazole). If a ring is specified as a long chain of atoms, then a change in any one of the bonds or angles will change the length of the ring closure bond, thus resulting in a very strongly coupled coordinate system. The second coordinate system for each case is less strongly coupled (or for C_5 makes better use of symmetry).

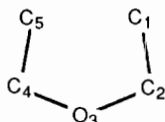*Example 8.* Strongly coupled coordinate systems for 5 membered rings

(a) C5 (D5h symmetry)

```
C
C 1 R
C 2 R 1 108.
C 3 R 2 108. 1 0.
C 4 R 3 108. 2 0.
```
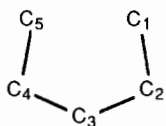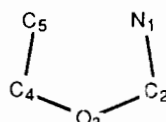
(b) C4O (C2v symmetry)

```
C
C 1 R1
O 2 R2 1 A2
C 3 R2 2 A3 1 0.
C 4 R1 3 A2 2 0.
```
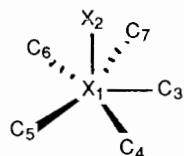
(c) C3NO (Cs symmetry)

```
N
C 1 R1
O 2 R2 1 A2
C 3 R3 2 A3 1 0.
C 4 R4 3 A4 2 0.
```


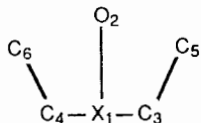*Example 9.* Less coupled coordinate systems for 5 membered rings

(a) C5 (D5h symmetry)

```
X
X 1 1.0
C 1 R 2 90.
C 1 R 2 90. 3  72.
C 1 R 2 90. 3 144.
C 1 R 2 90. 3 216.
C 1 R 2 90. 3 288.
```
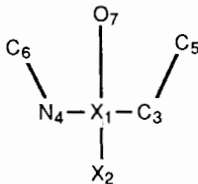
(b) C4O (C2v symmetry)

```
X
O 1 R1
C 1 R2 2 90.
C 1 R2 2 90. 3 180.
C 3 R3 1 A3  2 0.
C 4 R3 1 A3  2 0.
```

(c) C3NO (Cs symmetry)

```
X
X 1 1.0
C 1 R1 2 90.
N 1 R1 2 90. 3 180.
C 3 R2 1 A2  2 180.
C 4 R3 1 A3  2 180.
O 1 R4 3 A4  2 180.
```


Loose complexes can also cause problems for optimization programs, in part because of the large changes in geometry that often occur during their optimization. It is important that the 2 (or more) molecules in the complex have the necessary rotational and translational freedom relative to each other (to the extent allowed by the symmetry of the complex), as shown in Example 10. Furthermore, the coordinates for the relative motion should not be coupled to any other coordinates. Even with these precautions, it may be necessary to freeze the internal degrees of freedom and optimize the interfragment modes first, before optimizing all coordinates of the complex at the same time.

Example 10. Symbolic Z-matrix for the SIHF - - HCl cluster

```
Si
H 1 RH
F  1 RF      2 AF
Cl 1 RCL    3 ACL   2 BCL
H  4 RHCL 1 AHCL 3 BHCL
```
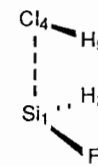

Strong coupling between coordinates can be particularly troublesome in transition structure optimizations. As far as possible, the transition vector should be dominated by only a few coordinates (preferably 1 or 2). The coupling between the coordinates of the transition vector and the remaining coordinates should also be as small as possible. Two coordinate systems for HCN isomerization are shown in Example 11. In the first case, the transition vector involves both the HCN bend and the CH stretch, but in the second case the transition vector is predominantly the XH displacement.

Example 11. Symbolic Z-matrices for the HCN $\rightarrow$ HNC transition state
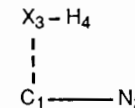
(a) simple coordinates

```
C
N  1 RCN
H  1 RCH  2  AHCH
```
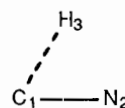
(b) better coordinates

```
C
N  1 RCN
X  1 RCX  2  90.
H  3 RXH  1  90. 2 0.
```


For some reactions, the coordinate system is easy to set up. For S_N2 reactions, abstractions and one center addition reactions, the transition vector is dominated by the bonds being made or broken. For other reactions, such as insertions, eliminations and cycloadditions, the choice of coordinates is less clear. These combine the difficulties of cyclic structures and loose complexes with the problems of transition states. In the elimination of H_2 from H_2CO, Example 12, the hydrogens could be specified by distances to the carbon and angles to CO; however, a small rotation of H_2 would require the concerted change of 2 distances and 2 angles. The alternate coordinate system avoids this problem and also reduces the coupling to the transition vector (primarily CX and XH stretch). Example 13 deals with the 1,2 cycloaddition of H_2 to N_2H_2. In this case symmetry is used to construct a less coupled coordinate system by locating the dummy atoms on the C_2 axis (as discussed in Section 5).

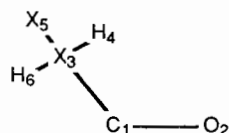*Example 12.* Symbolic Z-matrices for the $H_2CO \rightarrow H_2 + CO$ transition state

(a) simple coordinates

```
C
O 1 RCO
H 1 RCH1 2 ACH1
H 1 RCH2 2 ACH2
```
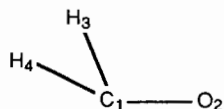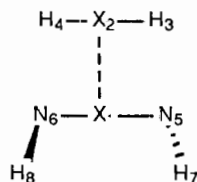
(b) better coordinates

```
C
O 1 RCO
X 1 RCX 2 AOCX
H 3 RXH 1 ACXH 2 0.
X 3 1.0   4 90.    1 180.
H 3 RXH 5 90.    4 180.
```


Example 13. Symbolic Z-matrix for the $H_2 + N_2H_2 \rightarrow N_2H_4$ transition state

```
X
X 1 RXX
H 2 RXH 1 90.
H 2 RXH 1 90. 3 180.
N 1 RXN 2 90. 3    0.
N 1 RXN 2 90. 3 180.
H 5 RNH 1 ANH 2 BNH
H 6 RNH 1 ANH 2 BNH
```


8. Initial Guess for Bond Lengths and Angles

One of the simplest ways to speed up an optimization is to make a good estimate of the geometry. Initial values for bond lengths and angles can be obtained from a number of sources:

(a) Standard geometries. There are various compilations of standard bond lengths and angles for a wide range of equilibrium structures [34, 35]. With a bit of chemical intuition and VSEPR theory, these standard values can be adjusted to give better estimates. It is not possible to construct a set of standard values of similar quality for the coordinates undergoing changes in transition states. However, concepts such as conservation of bond order, bond order-bond energy relations and the Pauling relation between bond length and bond order may be quite helpful.

(b) Empirical force field calculations. Although the range of molecules and the types of bonds can be somewhat limited, molecular mechanics calculations give good estimates of the optimized geometry for energy minima [36], especially of cyclic systems and cases where steric interactions are important. However, some care is needed with these methods in situations where electronic factors control the geometry.

(c) Semi-empirical MO calculations. Some semi-empirical MO programs predict optimized geometries as well as minimal basis set ab initio calculations. Known defects of various methods [29, 37, 38] should be taken into account when using semi-empirically optimized geometries for ab initio calculations.

(d) Lower level ab initio calculations. The various shortcomings of smaller basis sets [1] should be taken into account when scaling to calculations with larger basis sets and/or electron correlation.

(e) Quantum chemical data bases. Quite a wide variety of molecules have been optimized over the past decade or two. A large number of structures are available in machine readable and searchable form in the Carnegie-Mellon Quantum Chemistry Archive [3]. Many other calculations are referenced in Quantum Chemical Literature Data Base [2], also available on-line. The molecule may have already been optimized at the desired level of theory or at a lower level. Alternatively, these data bases are an excellent source for fragment geometries from which the molecule in question can be constructed.

(f) Experiment. X-ray, microwave and electron diffraction structures are highly desirable starting points for geometry optimizations, but frequently are not available for the structures studied theoretically.

9. Getting Close to the Transition Structure

Often a transition structure can be optimized directly without any problems, especially if the initial estimate of the Hessian has a suitable negative eigenvalue with an eigenvector that is a reasonable estimate to the transition vector (see Section 11). However, convergence to a transition state may sometimes require a better starting geometry than an optimization of a minimum. For difficult cases, standard geometries and chemical intuition may not yield estimates that are good enough for a direct transition structure optimization. Various techniques for getting close to a transition structure have been discussed in the literature (for leading references see [23]). A few of the methods are summarized below in order of increasing sophistication..

(a) Potential surface scan. If there is some doubt about the location of a saddle point along a reaction path, a series of energy only or energy + gradient calculations may be sufficient to locate the region of the transition state approximately. If more than one coordinate is important in the reaction path, a small grid of points may have to be calculated.

(b) Linear synchronous transit (LST) [39]. In this approach, the reaction path is approximated as a straight line in the space of interatomic distances (this may correspond to a curved path in Cartesian coordinates or internal coordinates). An estimate of the transition structure is obtained by finding the maximum along this one dimensional path. Since the true reaction path usually differs from the LST path, the LST estimate of the transition state is normally higher in energy than the true transition state, and may be outside the quadratic region of the true transition state. However, if a minimization is carried out perpendicular to the reaction path (akin to quadratic synchronous transit), a better estimate of the transition state can be obtained.

(c) Coordinate driving, walking up valleys and eigenvector following methods [40-42]. These methods attempt to follow the reaction path uphill toward the transition structure. In the coordinate driving approach, a coordinate dominating the reaction path is incremented at each step and the remaining coordinates are minimized. In the eigenvector following approach, steps are taken in the uphill direction along a selected eigenvector (usually the one with the lowest eigenvalue). This approach can be quite costly, if the method requires the Hessian to be recomputed frequently. The idea in both methods is to construct a path of shallowest ascent toward the transition structure.

However, both methods can miss the transition state, if it is not on the shallowest ascent path (see [23] for examples).
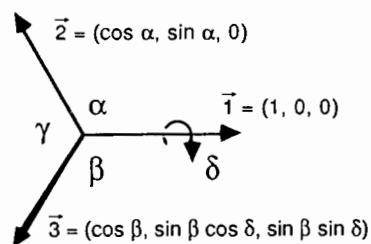
Once a reasonable initial estimate has been obtained for the transition structure, a suitable gradient optimization method [43-48] can be used to find the optimized geometry. If the initial estimate has been obtained by a potential surface scan or a linear synchronous transit calculation, it may be preferable to optimize the transition structure in 2 (or more) phases. First, the coordinates corresponding to the transition vector are frozen and the remaining coordinates are minimized. This brings the molecule closer to the reaction path. The second step is a full transition structure optimization with all coordinates varied. Some of the hill climbing and eigenvector following methods incorporate the equivalent of a direct gradient optimization as a final step.

10. Converting Between Different Z-Matrices

In setting up a calculation or during the course of an optimization, it is sometimes necessary to convert from one set of internal coordinates to another (e.g. the experimental geometry may be specified in an inconvenient coordinate system, or an attempt at optimization may reveal a strong coupling between coordinates). If the Cartesian coordinates are available, it is straight forward, but tedious, to determine the new internal coordinates manually. Alternatively, there are some programs that construct a new Z-matrix automatically [32b]. Most general purpose molecular modelling programs can also be used to calculate bond lengths and angles from the Cartesian coordinates. However, there may be some circumstances in which it is necessary or more convenient to interconvert a few valence and dihedral angles manually.

Schemes 1 and 2 show the construction of 2 of the more frequently used relations between valence and dihedral angles. In both cases, the Cartesian coordinates of appropriate fragments are constructed by rotating unit vectors by the required angles about particular axes. The desired angles are then obtained by simple dot products. Scheme 1 deals with the angles about a non-planar tricoordinate center or a tetracoordinate center: given valence angles α, β and γ, find dihedral angle δ, or given α, β and δ, find γ. Vector 1 is placed on the x axis (1, 0, 0); vector 2 is obtained by rotating vector 1 by α about the z axis (i.e. in the x,y plane) to give (cos α, sin α, 0). Vector 3 is obtained by rotating vector 1 by β about the z axis (cos β, sin β, 0), followed by δ about the x axis to give (cos β, sin β cos δ, sin β sin δ). The dot product between vectors 2 and 3 is the cosine of the third valence angle, γ. If needed, the resulting expression for cos γ can be solved for any of the other angles.

Scheme 1

$\vec{2} = (\cos \alpha, \sin \alpha, 0)$

$\vec{1} = (1, 0, 0)$

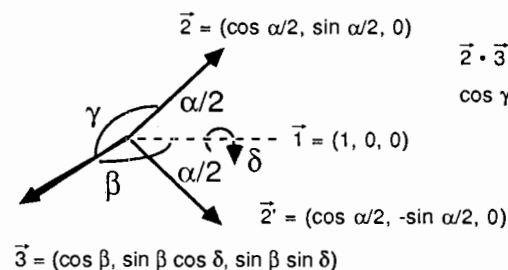$\vec{3} = (\cos \beta, \sin \beta \cos \delta, \sin \beta \sin \delta)$

$\vec{2} \cdot \vec{3} = \cos \gamma$

$\cos \gamma = \cos \alpha \cos \beta + \sin \alpha \sin \beta \cos \delta$

$\cos \delta = (\cos \gamma - \cos \alpha \cos \beta) / (\sin \alpha \sin \beta)$

Scheme 2 deals with the more specialized case when a plane or axis bisects an angle. The analysis proceeds as before, but with the bisector placed on the axis. If the planes of the angles α and β are perpendicular, a particularly simple expression is obtained: cos γ = cos $\alpha/2$ cos β. Many other relations can be derived in the same manner. The key is to place the right vector on the axis so that the remaining vectors can be generated by simple rotations about axes.

Scheme 2

$\vec{2} = (\cos \alpha/2, \sin \alpha/2, 0)$

$\vec{1} = (1, 0, 0)$

$\vec{2}' = (\cos \alpha/2, -\sin \alpha/2, 0)$

$\vec{3} = (\cos \beta, \sin \beta \cos \delta, \sin \beta \sin \delta)$

$\vec{2} \cdot \vec{3} = \cos \gamma$

$\cos \gamma = \cos \alpha/2 \cos \beta + \sin \alpha/2 \sin \beta \cos \delta$

11. Estimating the Hessian

Like the choice of internal coordinate systems and the starting geometry, the initial estimate of the Hessian can strongly influence the rate of convergence of an optimization. As indicated in eq (3), the next estimate of the optimized geometry depends on the Hessian. The better the initial Hessian, the better the predicted geometry and fewer steps needed to converge to the optimized geometry (the final optimized geometry, of course, is independent of the Hessian). At each step in the optimization, the approximate Hessian is updated, so that it eventually approaches the correct Hessian. Thus, with a poor initial Hessian, many of the optimization steps are needed just to improve the Hessian.

For a minimization, the initial Hessian must at least be positive definite (i.e. no zero or negative eigenvalues). For a transition structure or first order saddle point, a Hessian must have one and only one negative eigenvalue, and the corresponding eigenvector must be a reasonable approximation to the transition vector. Several alternatives are available for estimating the initial Hessian (most are automated in the more flexible MO programs). In order of increasing cost, these include:

(a) Unit matrix (or a unit matrix scaled by a constant). This contains no useful structural data about the molecule. Information about the stiffness or flexibility of various modes and the coupling between coordinates must be accumulated via the Hessian updating scheme during the course of the optimization. This will increase the number of optimization steps substantially. A (scaled or unscaled) unit is unsuitable for a saddle point optimization because it does not provide an estimate of the transition vector.

(b) Empirical force field Hessian. Molecular mechanics force fields can be quite good for minima, but the types of molecules and bonding situations treated by these force fields can be somewhat limited. A less accurate but more general scheme for estimating the Hessian from a simple valence force field has been used successfully

for minimizations [49]. No empirical force field is sufficiently general and reliable for transition states.

(c) Semi-empirical Hessians. Hessians calculated by semi-empirical MO methods are generally quite reasonable. Usually the Hessian must be scaled if it is used for ab initio calculations, since semi-empirical methods over-estimate some terms and underestimate others. A bit of caution is necessary for transition structures, because the geometry (and hence also the Hessian) for some transition structures optimized by semi-empirical methods can be rather different from those computed by ab initio methods.

(d) Numerical calculation of key elements of the Hessian. Gradient calculations at small displacements from the initial geometry can be used to calculate the more important rows and columns of the Hessian. For transition structure optimizations, it is essential that these include the coordinates that dominate the transition vector.

(e) Calculation of the full Hessian. The full Hessian can be calculated analytically or by numerically differentiating the gradients. The Hessian can be calculated at the same level as the optimization or with a smaller basis set (or at the SCF level for an optimization with correlation). Alternatively (but less accurate), the approximate Hessian from a lower level optimization on the same structure can be used.

(f) Recalculation of the full Hessian at each step in the optimization. This is the most expensive option, but may be necessary in a few of the most difficult cases.

12. Testing Stationary Points

Any stationary point found in an optimization should be tested to be sure that it has the proper number of imaginary frequencies or negative eigenvalues of the Hessian: i.e. 0 for a minimum and 1 for a transition state or first order saddle point. This is done by computing the full Hessian, either analytically or numerically, and diagonalizing the matrix or computing the vibrational frequencies. Note that the approximate Hessian obtained by an updating procedure in an optimization is not sufficiently accurate to test a stationary point. Furthermore, it does not contain any information about displacements to lower symmetry structures. If the stationary point has the wrong number of negative eigenvalues [50], a lower energy stationary point with the right number of negative eigenvalues can be found by distorting the molecule along the offending eigenvector and re-optimizing. Often this leads to a structure with lower symmetry and requires the Z-matrix to be rewritten in a lower symmetry form.

If the potential energy surface is not too flat, it has been common practice to test a stationary point at one level of calculation and assume that the addition of more basis functions and/or electron correlation does not change the nature of the stationary point. Weakly bound complexes, very flexible transition states and structures with strong configurational mixing can provide exceptions to this practice. If there is any doubt, the stationary point should be tested at the highest level of calculation used for the optimization.

For transition structures, it is also important to check the nature of the eigenvector with the negative eigenvalue to be sure that the saddle point connects the correct reactants and products. For some reactions, especially those involving non-least motion pathways, it may not be immediately obvious from the transition vector that the appropriate saddle point for the reaction has been found. In such cases, it may be necessary to follow the reaction path part of the way from the saddle point toward the reactants and toward the products to verify that the transition state is on the correct reaction path. A number of

algorithms for reaction path following have been published [51-55]. The most efficient method for following paths by MO calculations appears to be a recent method by Gonzalez and Schlegel [55].

13. Things to Try When Optimizations Fail

Optimizations misbehave for a variety of reasons. Listed below are a number of conditions that can be encountered during a minimization or a search for a saddle point. Some optimizers check for these problems, reporting them when they occur and stopping if necessary. Other optimizers struggle to continue and may terminate without warnings or diagnostics when the situation becomes hopeless. For conditions listed below, some possible causes are given and some remedies are suggested (however, there are no guaranties that the remedies will work).

Forces too large While this is not normally a problem, it may signal an error in the input: (a) the starting geometry may be poor, or (b) the coordinate system may be badly chosen, causing the optimizer to predict a poor geometry. Either get a better starting guess for the geometry or reconstruct the Z-matrix to avoid the strong coupling that caused the optimization to take a bad step.

Negative eigenvalues of the Hessian during a minimization This indicates that (a) the structure is not a minimum, or (b) numerical problems occurred in updating the Hessian. For (a), displace along the offending eigenvector to get to a lower energy structure and continue the optimization. For (b), restart the optimization with a better estimate of the Hessian. If the problem persists, it may be necessary to freeze the coordinates that dominate the vector with the negative eigenvalue. When the remaining coordinates have converged, the frozen variables can be released so that all coordinates can be optimized simultaneously.

Too many negative eigenvalues of the Hessian during a transition structure optimization Either (a) the optimization is converging on a second order saddle point, or (b) there are numerical problems with the Hessian. In case (a), examine the eigenvectors with the negative eigenvalues and choose one that does not correspond to the transition vector for the desired reaction; displace along this eigenvector until a minimum is found and restart the transition structure optimization from the new geometry with a new estimate of the Hessian (e.g. re-compute the Hessian elements for the displaced coordinates). The remedy for case (b) is the same as above - restart with a better estimate of the Hessian. Like with minimizations, if the problems persist, it may be necessary to freeze a few of the more flexible coordinates until the optimization gets closer to the saddle point.

No negative eigenvalues of the Hessian during a transition structure optimization There are 2 possible causes: (a) the structure is not a saddle point or is not sufficiently close to the quadratic region of the saddle point, or (b) there are numerical problems with the Hessian. For (a), any of the methods for getting closer to the transition state can be tried (Section 9): (i) linear synchronous transit (starting from the current structure plus a corresponding structure on the other side of the transition state), (ii) coordinate driving (several steps of increment the coordinate dominating the reaction path and minimizing of the rest of the coordinates) or (iii) eigenvector following (choose the appropriate eigenvector and use one of the hill climbing algorithms to follow the path of shallowest ascent toward the transition structure). Once a more suitable starting structure has been found, one of the direct methods for transition structure optimization can be used. The remedy for case (b) is the same as above - restart with a better estimate of the Hessian.

Eigenvalue of the Hessian too large While this is not normally a problem, it may signal an error in the input. This may be due to (a) a bad initial Hessian (get a better estimate), (b) a bad update of the Hessian (restart with a new estimate of the Hessian) or (c) a strongly coupled coordinate system (reconstruct the Z-matrix to avoid the strong coupling).

Eigenvalue of the Hessian too small There are a number of possible causes for this problem: (a) the molecule is actually in a shallow minimum and should have small eigenvalues, (b) there is a redundancy in the choice of internal coordinates or (c) there are numerical problems with the Hessian. For (a) it may be necessary to tighten the convergence criteria (e.g. RMS gradient) as well as the optimization control parameters (like the test for small eigenvalues). Case (b) is the more likely problem and requires that the Z-matrix be reconstructed to remove the redundancy (see Section 6). The remedy for (c) is to restart with a better estimate of the Hessian.

Number of steps exceeded The possibilities are: (a) it really is a difficult optimization and needs more steps, (b) there is a redundancy in the internal coordinates (fix the Z-matrix and restart), (c) there are some very loose coordinates that are slowing the optimization (freeze the loose coordinates until the others have converged, then unfreeze the coordinates and optimize everything), (d) there is strong coupling in the coordinate system (restructure the Z-matrix and restart the optimization), or (e) the initial estimate of the Hessian was quite poor (recalculate a few of the elements of the Hessian and continue the optimization).

Maximum step size exceeded If the step size is larger than the trust radius, most optimizers scale the step to the appropriate length. If this occurs frequently, it may be indicative of a small eigenvalue in the Hessian; the causes and remedies for this have been discussed above.

Step size too small, optimization goes nowhere despite sizeable gradients This could be due to: (a) too small a trust radius, (b) tightly coupled coordinates and/or a very non-quadratic energy surface, or (c) a Hessian with some spuriously large matrix elements. Case (a) is probably caused by inappropriate updating of the trust radius; hence this feature should be temporarily disabled and the optimization continued. The remedy for (b) is to reconstruct the Z-matrix to avoid the strong coupling and to simplify the behavior of the energy surface. Case (c) can be overcome by continuing the optimization with an improved estimate of the Hessian.

Change in point group detected during an optimization Either (a) the Z-matrix does not reflect the full symmetry of the molecule and the optimization has inadvertently distorted the molecule (fix the Z-matrix and restart the optimization), or (b) the molecule has C_s or C_2 symmetry and the principle axes have changed order (continue the optimization, possibly with symmetry suppressed).

Conclusions

This Chapter has attempted to discuss some of the practical problems of geometry optimization. Though optimization algorithms vary from MO program to MO program, they share a number of features and shortcomings. The 3 areas of input that most affect the performance of a given geometry optimization algorithm are: (a) the choice of internal coordinates (redundancy and strong coupling must be avoided), (b) the starting geometry, and (c) the initial estimate of the Hessian. Symmetry, the use of dummy atoms, coordinate redundancy, strong coupling among coordinates, conversion between coordinate systems and testing of stationary points have been considered in some detail. Finally, some of the conditions that cause optimizations to misbehave have been discussed and some remedies have been suggested. Although much of the discussion draws on experience with the

GAUSSIAN series of programs, the concepts and suggestions should be applicable to most geometry optimizations and transition structure searches based on internal coordinates.

Appendix: Optimization, Searching and Numerical Differentiation Links in GAUSSIAN

L101 Symbolic Z matrix input .

L102 Fletcher-Powell minimization method using only the energy [56].

L103 Berny optimization method for equilibrium geometries and transition structures [43].

L105 Murtagh-Sargent minimization method using gradients [57].

L106 Calculation of the Hessian by numerical differentiation of the gradients.

L107 Linear synchronous transit (requires only the energy) [39].

L108 Potential surface scan.

L109 Fixed metric optimization for equilibrium geometries and transition structures using gradients obtained by numerical differentiation of the energy.

L110 Calculation of the Hessian by numerical second derivatives of the energy.

L111 Calculation of hyperpolarizabilities by numerical second derivatives of the dipole moment.

L113 Eigenvector following algorithm using numerical gradients [42].

L114 Eigenvector following algorithm using analytical gradients [42].

L115 Reaction path following using gradients [55].

References

1. Hehre, W. J., Radom, L., Schleyer, P. vR., and Pople, J. A., *Ab Initio Molecular Orbital Theory*, Wiley-Interscience, New York, 1986.

2. Ohno, K., and Morokuma, K., *Quantum Chemistry Literature Data Base*, Elsevier, Amsterdam, 1982; yearly supplements published in special issues of the journal *J. Mol. Struct./Theochem.*; on-line version available through Japan Assoc. for International Chemical Information.

3. Whiteside, R. A., Frisch, M. J., and Pople, J. A., *The Carnegie-Mellon Quantum Chemistry Archive*, 3rd Ed., Carnegie-Mellon University, Pittsburgh, 1983; current version available on-line from Gaussian, Inc.

4. Frisch, M. J., Binkley, J. S., DeFrees, D. J., Raghavachari, K., Schlegel, H. B., Whiteside, R. A., Fox, D. J., Martin, R. L., Fluder, E. M., Melius, C. F., Kahn, L. R., Stewart, J. J. P., Bobrowicz, F. W., and Pople, J. A., *GAUSSIAN 86*, Carnegie-Mellon Publishing Unit, Pittsburgh, 1984, and subsequent releases.

5. Pulay, P., *Adv. Chem. Phys.*, **69**, 241 (1987).

6. Jørgensen, P., and Simons, J. (Eds.), *Geometrical Derivatives of Energy Surfaces and Molecular Properties*, Reidel, Dordrecht, 1986.

7. Gaw, J. F., and Handy, N. C., *Annu. Rep. Prog. Chem. Sec. C*, **81**, 291 (1985).

8. Fogarasi, G., and Pulay, P., *Annu. Rev. Phys. Chem.*, **35**, 191 (1984).

. Fitzgerald, G., Harrison, R., Laidig, W. D., and Bartlett, R. J., *J. Chem. Phys.*, **82**, 4379 (1985).

0. Gauss, J., and Cremer, D., *Chem. Phys. Lett.*, **138**, 131 (1987).

1. Krishnan, R., Schlegel, H. B., and Pople, J. A., *J. Chem. Phys.*, **72**, 4654 (1980); Brooks, B. R., Laidig, W. D., Saxe, P., Goddard, J. D., Yamaguchi, Y., and Schaefer, H. F., *J. Chem. Phys.*, **72**, 4652 (1980); Osamura, Y.; Yamaguchi, Y., and Schaefer, H. F., *J. Chem. Phys.*, **77**, 383 (1982); Rice, J. E., Amos, R. D., Handy, N. C., Lee, T. J., and Schaefer, H. F., *J. Chem. Phys.*, **85**, 963 (1986); Shepard, R., *Int. J. Quantum Chem.*, **31**, 33 (1987).

2. Scheiner, A. C., Scuseria, G. E., Rice, J. E., Lee, T. J., and Schaefer, H. F., *J. Chem. Phys.*, **87**, 5361 (1987); Fitzgerald, G., Harrison, R., Laidig, W. D., and Bartlett, R. J., *Chem. Phys. Lett.*, **117**, 433 (1985); Adamowicz, L., Laidig, W. D., and Bartlett, R. J., *Int. J. Quantum Chem. Symp*, **18**, 245 (1984).

3. Kato, S., and Morokuma, K., *Chem. Phys. Lett.*, **65**, 19 (1979); Goddard, J. D., Handy, N. C., and Schaefer, H. F., *J. Chem. Phys.*, **71**, 1525 (1979); Schlegel, H. B., and Robb, M. A., *Chem. Phys. Lett.*, **92**, 43 (1982); Knowles, P. J., Sexton, G. J., and Handy, N. C., *Chem. Phys.*, **72**, 337 (1982); Taylor, P. R., *J. Comput. Chem.*, **5**, 589 (1984).

4. Pople, J. A., Krishnan, R., Schlegel, H. B., and Binkley, J. S., *Int. J. Quantum Chem. Symp*, **13**, 225 (1979).

15. Handy, N. C., Amos, R. D., Gaw, J. F., Rice, J. E., Simandiras, T. J., Lee, T. J., Harrison, R. J., Laidig, W. D., Fitzgerald, G., and Bartlett, R. J., in ref. [6]; Handy, N. C., Amos, R. D., Gaw, J. F., Rice, J. E., and Simandiras, T. J., *Chem. Phys. Lett.*, **120**, 151 (1985).

16. Lee, T. J., Handy, N. C., Rice, J. E., Scheiner, A. C., and Schaefer, H. F., *J. Chem. Phys.*, **85**, 3930 (1986).

17. Camp, R. N., King, H. F., McIver, J. W., and Mullally, D., *J. Chem. Phys.*, **79**, 1088 (1983); Hoffman, M. R., Fox, D. F., Gaw, J. F., Osamura, Y., Yamaguchi, Y., Grev, R. S., Fitzgerald, G., Schaefer, H. F., Knowles, P. J., and Handy, N. C., *J. Chem. Phys.*, **80**, 2660 (1984); Page, M., Saxe, P., Adams, G. F., and Lengsfield, *J. Chem. Phys.*, **81**, 434 (1984)

18. Gaw, J. F., Yamaguchi, Y., and Schaefer, H. F., *J. Chem. Phys.*, **81**, 6395 (1984); Gaw, J. F., Yamaguchi, Y., Schaefer, H. F., and Handy, N. C., *J. Chem. Phys.*, **85**, 5132 (1986); Gaw, J. F., Yamaguchi, Y., Remington, R. B., Osamura, Y., and Schaefer, H. F., *Chem. Phys.*, **109**, 237 (1986); Schaefer, H. F., and Yamaguchi, Y., *J. Mol. Struct.*, **135**, 369 (1986); Gaw, J. F., and Handy, N. C., in [6].

19. Duran, M., Yamaguchi, Y., Osamura, Y., and Schaefer, H. F., *J. Mol. Struct.*, **163**, 389 (1988).

20. Pulay, P., *J. Chem. Phys.*, **78**, 5043 (1983); Almlöf, J., and Taylor, P. R., *Int. J. Quantum Chem.*, **27**, 743 (1985).

21. Jørgensen, P., and Simons, J. *J. Chem. Phys.*, **79**, 334 (1983).

22. Schlegel, H. B., in *Computational Theoretical Organic Chemistry* (Eds. Csizmadia, I. G., and Daudel, R.), Reidel, Dordrecht, 1981.

23. Schlegel, H. B., *Adv. Chem. Phys.*, **67**, 249 (1987).

24. Bell, S., and Crighton, J. S., *J. Chem. Phys.*, **80**, 2464 (1984).

25. Head, J. D., Weiner, B., and Zerner, M. C., *Int. J. Quantum Chem.*, **33**, 177 (1988).

26. Scales, L. E., *Introduction to Non-linear Optimization*, MacMillan, Basingstoke, 1985.

27. Fletcher, R., *Practical Methods of Optimization*, Wiley, Chichester, 1981.

28. Gill, P. E., Murray, W., and Wright, M. H., *Practical Optimization,* .Academic Press, New York, 1982; Powell, R., *Non-linear Optimization,* Academic Press, New York, 1982.

29. Clark, T., *A Handbook of Computational Chemistry*, Wiley-Interscience, New York, 1985.

30. Stanton, R. E., and McIver, Jr, J. W., *J. Am. Chem. Soc.*, **97**, 3632 (1975).

31. Thiel, W., *J. Mol. Struct.*, **163**, 415 (1988).

32. (a) The author wishes to thank Dr. M. J. Frisch for the guidelines for using symmetry to place dummy atoms. These algorithms have been incorporated in the program NewZmat [33b]; (b) Frisch, M. J., *NewZmat*, 1986.

33. Pople, J. A., *J. Am. Chem. Soc.*, **102**, 4615 (1980); Pople, J. A., Sataty, Y. A., and Halevi, E. A., *Israel J. Chem.*, **19**, 290 (1980).

34. Pople, J. A., and Gordon, M. S., *J. Am. Chem. Soc.*, **89**, 4253 (1967); Radom, L., Hehre, W. J., and Pople, J. A, *J. Am. Chem. Soc.*, **93**, 289 (1971).

35. Peterson, M. R., and Csizmadia, I. G., *J. Mol. Struct.*, **125**, 399 (1985).

36. Burkert, U., and Allinger, N. L., *Molecular Mechanics*, American Chemical Society, 1981.

37. Sadlej, J., (Cooper, I. L., transl. ed.) *Semi-empirical Methods of Quantum Chemistry*, Ellis Horwood, Chichester, 1985.

38. Segal, G. A., *Semi-empirical Methods of Electronic Structure Calculation*, (Modern Theoretical Chemistry Vol. 7 and 8) Plenum, New York, 1977.

39. Halgren, T. A., and Lipscomb, W. N., *Chem. Phys. Lett.*, **49**, 225 (1977).

40. Cerjan, C. J., and Miller, W. H., *J. Chem. Phys.*, **75**, 2800 (1981); Simons, J. Jørgensen, P., Taylor, H., and Ozment, J., *J. Chem. Phys.*, **87**, 2745 (1983); Nguyen, D. T., and Case, D. A., *J. Phys. Chem.*, **89** 4020 (1985); Banerjee, A., Adams, N., Simons, J., and Shepard, R., *J. Phys. Chem.*, **89** 52 (1985).

41. Hoffman, D. K., Nord, R. S., Ruedenberg, K., *Theor. Chim. Acta.*, **69**, 265 (1986); Jørgensen, P., Jensen, H. J. A., and Helgaker, T., *Theor. Chim. Acta.*, **73**, 55 (1988)

42. Baker, J., *J. Comput. Chem.*, **7**, 385 (1986).

43. Schlegel, H. B., *J. Comput. Chem.*, **3**, 214 (1982).

44. Scharfenberger, P., *J. Comput. Chem.*, **3**, 277 (1982).

45. Tapıa, O., and Andrés, J., *Chem. Phys. Lett.*, **109**, 471 (1984).

46. Bell, S., Crighton, J. S., and Fletcher, R., *Chem. Phys. Lett.*, **82**, 122 (1981).

47. Head, J. D., Weiner, B., and Zerner, M. C., *Int. J. Quantum Chem.*, **33**, 177 (1988).

48. Bálint, I., and Bán, M. I., *Theor. Chim. Acta.*, **63**, 255 (1983).

49. Schlegel, H. B., *Theor. Chim. Acta.*, **66**, 333 (1984).

50. Under some circumstances an imaginary frequency may also signal an instability in the wavefunction.

51. Ishida, K., Morokuma, K., and Komornicki, A., *J. Chem. Phys.*, **66**, 2153 (1977); Schmidt, M. W., Gordon, M. S., and Dupuis, M., *J. Am. Chem. Soc.*, **107**, 2585 (1985).

52. Müller, K., and Brown, L. D., *Theor. Chim. Acta.*, **53**, 75 (1979).

53. Garrett, B. C., Redmon, M. J., Steckler, R., Truhlar, D. G., Baldridge, K. K., Bartol, D., Schmidt, M.W., and Gordon, M.S., *J. Phys. Chem.*, **92** 1476 (1988).

54. Page, M., and McIver, Jr, J. W., *J. Chem. Phys.*, **88**, 922 (1988).

55. Gonzalez, C., Schlegel, H. B., submitted; also described in ref [23].

56. Fletcher, R., and Powell, M. J. D., *Comput. J.*, **6**, 163 (1963); Davidon, W., *Argonne Nat. Lab. Report*, ANL-5990; Binkley, J. S., *J. Chem. Phys.*, **64**, 5142 (1976).

57. Murtagh, B. A., and Sargent, R. W. H., *Comput. J.*, **13**, 185 (1972).