AIP | The Journal of Chemical Physics

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Citation: J. Chem. Phys. **105**, 192 (1996); doi: 10.1063/1.471864
View online: http://dx.doi.org/10.1063/1.471864
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v105/i1
Published by the American Institute of Physics.

The generation and use of delocalized internal coordinates in geometry optimization

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(Received 2 February 1996; accepted 28 March 1996)

Following on from the earlier work of Pulay and Fogarasi [J. Chem. Phys. **96**, 2856 (1992)] we present an alternative definition of natural internal coordinates. This set of *delocalized internal coordinates* can be generated for any molecular topology, no matter how complicated, and is fully nonredundant. Using an appropriate Schmidt-orthogonalization procedure, all standard bond length, bond angle, and dihedral angle constraints can be imposed within our internal coordinate scheme. Combinatorial constraints (in which sums or differences of stretches, bends, and torsions remain constant) can also be imposed. Optimizations on some fairly large systems (50–100 atoms) show that delocalized internal coordinates are far superior to Cartesians even with reliable Hessian information available at the starting geometry. *© 1996 American Institute of Physics.* [S0021-9606(96)01525-5]

I. INTRODUCTION

The use of so-called ''natural internal coordinates'' in geometry optimization has now become widespread. These coordinates, first introduced into geometry optimization by Pulay *et al.*,[1] involve the use of *individual* bond displacements as stretching coordinates but *linear combinations* of bond angles and torsions as deformational coordinates. Suitable linear combinations of bends and torsions (the two are considered separately) are selected using group theoretical arguments based on local pseudosymmetry. For example, bond angles for an sp^3 hybridized carbon are all roughly tetrahedral regardless of the actual groups attached, and idealized tetrahedral symmetry can be used to generate deformational coordinates around the central carbon atom.

The major advantage of natural internal coordinates in geometry optimization is that they significantly reduce the coupling, both harmonic *and* anharmonic, between the various coordinates. This typically leads to a much smoother optimization and more rapid convergence than with a more coupled set of coordinates, such as Cartesian coordinates. Natural internals are in general also superior to Z-matrix internal coordinates, which describe the molecular geometry in terms of *individual* angles and torsions. Compared to natural internals, Z-matrix coordinates arbitrarily omit some angles and torsions—to prevent redundancy—and this can introduce strong coupling between the coordinates, especially with a poorly constructed Z matrix.

Having said all this however, it has been clearly demonstrated that for medium sized systems (say up to 30 atoms), with ''reasonable'' starting geometries and with a reliable initial Hessian (second derivative) matrix, optimization in Cartesian coordinates can be just as efficient as in both Z matrix[2] and natural internal coordinates.[3] In *ab initio* work a simple molecular mechanics force constant matrix is usually perfectly adequate as a starting Hessian, provided, of course, that one is available.

The same work[2,3] has also shown that, without the initial curvature information, optimization in Cartesian coordinates is extremely inefficient, especially for larger systems. With poor starting geometries, Cartesian coordinates are inferior to internal coordinates, even with an exact Hessian matrix available at every optimization cycle.[4]

Although they were first introduced over 15 years ago,[1] it is only in the past few years—with the development of computational algorithms capable of generating them automatically (again pioneered by Pulay and co-workers[5])—that natural internal coordinates have become popular. For *minimization* they are the coordinates of first choice.

There are, however, some disadvantages to natural internal coordinates, at least in the way they are commonly constructed and used.

First, algorithms for the automatic construction of natural internals are quite complicated. There are a large number of different structural possibilities, most of which have to be considered separately, and to adequately handle even the most common of these can take several thousand lines of code. In cases with a complex molecular topology, e.g., multiply fused rings and cage compounds, the assigning algorithm may simply be unable to generate a suitable set of coordinates.

Second, there is the problem of redundancy. For the more complex molecular topologies, most assigning algorithms generate more natural internal coordinates than the usual $3N-6$ (where N is the number of atoms) that are required to characterize the relative positions of the nuclei. The redundancies can be removed by eliminating appropriate coordinates, but—as with the omission of individual angles and

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torsions from a Z matrix—this can be somewhat arbitrary, and may not result in a good set of natural internals, especially if a large number of generated coordinates have to be omitted.

The redundancy problem has recently been addressed in an excellent paper by Pulay and Fogarasi,[6] who have developed a scheme for carrying out geometry optimization in the *redundant* coordinate space.

Following a brief review of the work of Pulay and Fogarasi,[6] we present in this article a greatly simplified scheme for generating a complete *nonredundant* set of ''natural internal coordinates.'' We argue that, in a certain mathematical sense, the internal coordinate set that we generate is the ''best'' possible set. Geometry optimization is carried out in the *nonredundant* coordinate space, which significantly reduces the calculational overhead, particularly in the transformation back to Cartesian coordinates after a new geometry has been calculated in the internal coordinate space.

Additionally we demonstrate how, by an appropriate Schmidt-orthogonalization procedure, standard fixed bond length, bond angle, and dihedral angle constraints can be implemented within this natural internal coordinate scheme. In this way we are able to marry the advantages of natural internals with the utility of being able to impose constraints on *individual* bond angles and torsions as provided by the Z-matrix approach (without the necessity of the user having to write his or her own Z matrix).

II. THEORY

A. Delocalized internal coordinates

Following Pulay and Fogarasi,[6] we consider a set of n internal coordinates $\mathbf{q}=(q_1,q_2,\ldots,q_n)^T$. Displacements $\Delta\mathbf{q}$ in $\mathbf{q}$ are related to the corresponding Cartesian displacements $\Delta\mathbf{X}$ by means of the usual B matrix[7]

$$\Delta\mathbf{q}=\mathbf{B}\Delta\mathbf{X}. \tag{1}$$

If any of the internal coordinates $\mathbf{q}$ are redundant, then the rows of the B matrix will be linearly dependent.

One way of removing redundancies amongst the coordinates is to form the corresponding row of the B matrix for a particular internal coordinate, Schmidt orthogonalize this against all the previous rows and reject the coordinate if a linear dependency (a zero vector) is found. Prior to this work, this was the approach used in the OPTIMIZE program[8] and it is also used in the natural internal coordinate scheme in the TURBOMOLE package.[9] However, as mentioned in the Introduction, this is rather arbitrary, as internal coordinates are kept (or rejected) simply in the order in which they are taken.

Another way in which the redundancies can be identified is to form the B matrix for *all* internal coordinates (keep *all* rows of the B matrix) and then form and diagonalize the $n\times n$ matrix $\mathbf{G}=\mathbf{B}\mathbf{B}^T$. Redundancies can be identified as eigenvectors of the $\mathbf{G}$ matrix with zero eigenvalues. This method is very clean, but has the side-effect that the readily identifiable nonredundant coordinates (those eigenvectors of $\mathbf{G}$ with eigenvalues >0) are now expressed as, in general, complicated linear combinations of the original coordinate set.

In Pulay and Fogarasi's scheme[6] the $\mathbf{G}$ matrix is formed and diagonalized but *all* coordinates—nonredundant *and* redundant—are kept. By using the generalized inverse, i.e., by diagonalizing $\mathbf{G}$, inverting only the nonzero eigenvalues, and transforming back, Pulay and Fogarasi are able to cast the entire optimization in terms of the *original* coordinate set, including the redundancies. Exactly the same transformations between Cartesian and internal coordinate quantities (e.g., gradient, Hessian) hold as for the nonredundant case, but with the generalized inverse replacing the regular inverse.

Judging from the examples given in Ref. 6, Pulay and Fogarasi intended their redundant optimization scheme as a supplement to their standard natural internal optimization approach. Any molecular system to be optimized would be given to the ''standard'' algorithms, a set of natural internal coordinates would be constructed in the normal manner, and any redundancies in the generated coordinate set would be handled by the new scheme.

Pulay and Fogarasi's work[6] immediately suggests an alternative approach. Natural internal coordinates are linear combinations of individual bond angles and torsions. Their very construction removes much of the redundancy amongst the individual—let us call them primitive—bends and torsions that comprise them. Since the remaining redundancy can easily be detected by forming and diagonalizing the $\mathbf{B}\mathbf{B}^T$ matrix, why not bypass the construction of natural internals altogether? Simply construct the B matrix directly out of the primitive internals (the *individual* bond lengths, angles, and torsions), form and diagonalize $\mathbf{B}\mathbf{B}^T$ and take the nonredundant eigenvectors as our working coordinate set, i.e., as a ''new'' definition of our ''natural internal coordinates.''

In detail, what we are proposing is as follows. We start by generating an initial set of primitive internal coordinates to describe the geometry of our molecule. At this stage it does not matter exactly what these are, as long as there is a well-defined recipe for obtaining them and they span all the degrees of freedom of the system under consideration. Our initial set of primitive internals is obtained solely on the basis of atomic connectivity, i.e., which atoms are considered bonded to one another. The connectivity can be given (e.g., from a graphical model builder) or determined from the input geometry by simple distance criteria. In general we consider just three types of primitive internal coordinate, namely all stretches, all planar bends, and all proper torsions that can be generated based on the atomic connectivity. (If three atoms are linear or near linear, the planar bend is replaced by two special bending coordinates, the coplanar, and perpendicular bends;[10] torsions involving these atoms are modified or ignored. Additionally we can also handled out-of-plane bends.) Let there be n such individual primitives forming our initial internal coordinate set $\mathbf{q}$. Note that there will typically be many more primitive internals than are necessary to describe the $3N-6$ degrees of freedom of a molecule containing N atoms.

We form the full B matrix for all n primitive internals. Many rows of our B matrix will be linearly dependent, but that is of no concern at this stage. We then form and diagonalize the $n \times n$ matrix $\mathbf{G=BB}^T$. Diagonalization of $\mathbf{G}$ results in two sets of eigenvectors; a set of $m=3N-6$ eigenvectors with eigenvalues $\lambda>0$ and a set of $n-m$ eigenvectors with eigenvalues $\lambda=0$ (to numerical precision). The eigenvalue equation of $\mathbf{G}$ can thus be written

$$\mathbf{G}(\mathbf{UR})=(\mathbf{UR})\begin{pmatrix}\mathbf{\Lambda} & \mathbf{0}\\ \mathbf{0} & \mathbf{0}\end{pmatrix}, \tag{2}$$

where $\mathbf{U}$ is the set of nonredundant eigenvectors of $\mathbf{G}$ (those with eigenvalues $\lambda>0$) and $\mathbf{R}$ is the corresponding redundant set. We can say that $\mathbf{U}$ spans the *nonredundant subspace* and $\mathbf{R}$ the *redundant subspace* of our original space of primitive internals $\mathbf{q}$. Note that we are using the term redundant in a more restrictive sense in this definition than hitherto. Previously—following Pulay and Fogarasi[6]—the term redundant was used to describe a *set* of coordinates which contained *more* coordinates than were necessary to describe all possible geometrical changes in the system, i.e., one or more of the coordinates were redundant (in the sense that the rows of the B matrix for this set of coordinates were linearly dependent). From here on an *individual* coordinate vector will be termed redundant if it lies in the redundant subspace $\mathbf{R}$ defined above.

Eigenvectors in both $\mathbf{U}$ and $\mathbf{R}$ will each be linear combinations of potentially *all* the original primitive internals. Despite this apparent complexity, we take the set of nonredundant eigenvectors $\mathbf{U}$ as our working set of ''natural internal coordinates.'' Since natural internal coordinates defined in this way are much more ''delocalized'' than those originally proposed by Pulay *et al.*,[1] we call this new set *delocalized internal coordinates*.

For an unconstrained optimization on a system with no symmetry, we simply take the set $\mathbf{U}$ exactly as obtained above as our *active coordinate set*. If the system has symmetry, then we can in general eliminate one or more additional coordinates, in which case our set of active coordinates will in turn be a subspace of the set of nonredundant coordinates. Our code can recognize and utilize all point group symmetry up to and including I_h .

This approach has several advantages over previous methods for generating natural internal coordinates:

(1) Several thousand lines of code, namely code used to generate natural internal coordinates by direct examination of the molecular topology, can be discarded, or—more to the point—if you are interested in using natural internals in geometry optimization but do not have access to generating code, need never be written.

(2) A set of internal coordinates suitable for use in geometry optimizations can be generated for essentially *any* molecular topology. This is in marked contrast to the ''direct examination'' algorithms which often have difficulty with, e.g., cage compounds and multiply fused rings.

(3) There are no problems separating nonredundant from redundant coordinates, and optimization can be carried out entirely in the nonredundant subspace.

One possible criticism against the use of delocalized internal coordinates defined in this way, namely that they are such a complicated ''mixing'' of the original primitive internals as to be a poor choice for use in an actual optimization, is entirely unfounded. On the contrary, we will argue that, in a certain sense, coordinates generated by the approach outlined are the ''best'' possible choice one could make.

Before proceeding further, and to help clarify our arguments, we consider an actual example, namely the set of internal coordinates generated for the fluoroethylene molecule. Relevant printout from the current code is shown in Scheme 1.

For fluoroethylene (Scheme 1) our primitive internal coordinate set comprises 5 stretches, 6 bends, and 4 torsions, giving a total of 15 primitive internals. Fluoroethylene has 12 internal degrees of freedom and so the primitive coordinate set has three redundancies. These redundancies are associated with those eigenvectors of the $\mathbf{BB}^T$ matrix with zero eigenvalues. A further three coordinates (those with components for the torsions) can be eliminated by symmetry, leaving the final set of nine nonredundant ''active'' vectors spanning all the internal degrees of freedom in planar fluoroethylene. This is the set of ''delocalized internal coordinates'' used to carry out the optimization. As can be seen (Scheme 1), each coordinate is a linear combination of all five stretches and all six bends (the torsions are eliminated by symmetry).

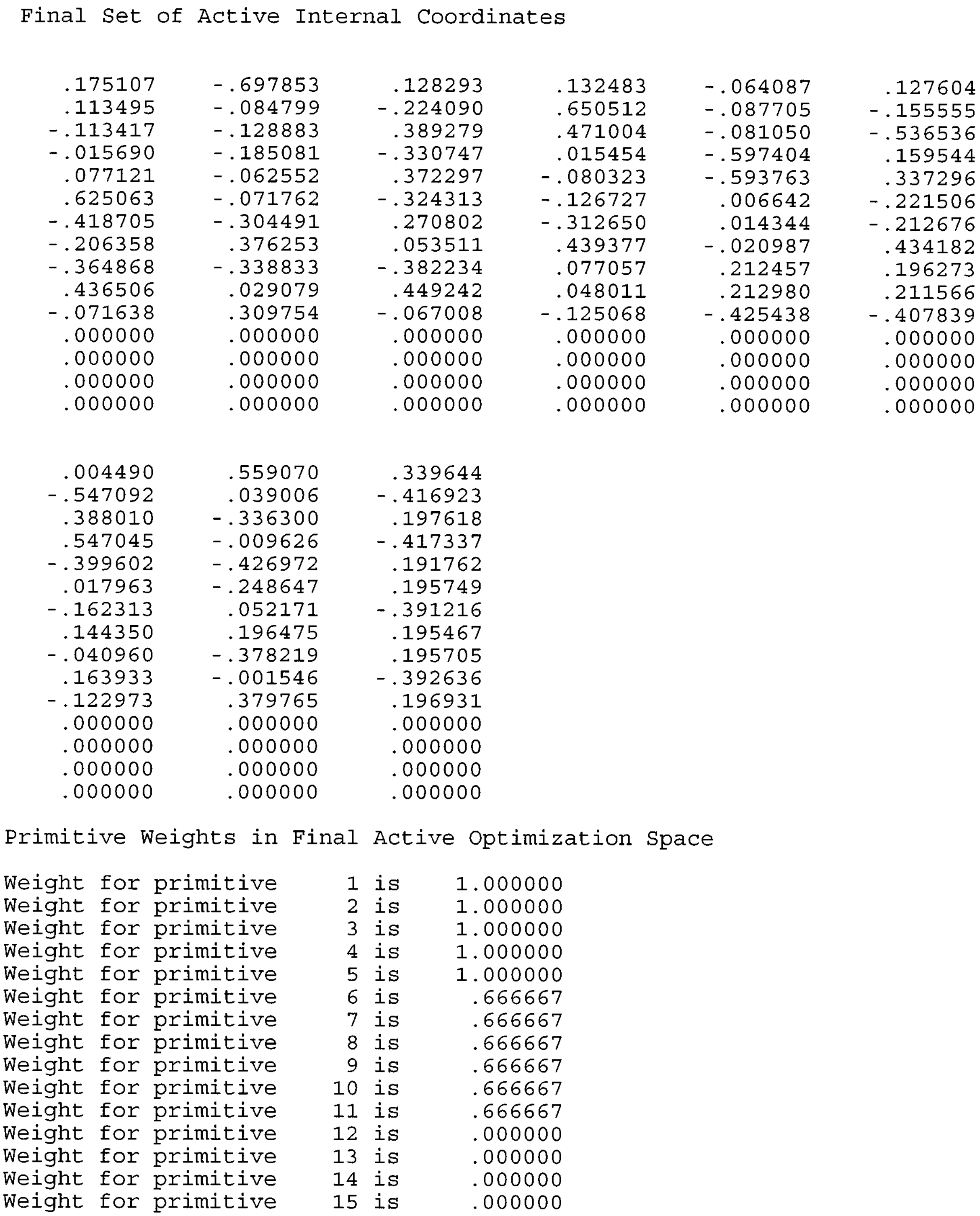
Also shown in Scheme 1 are the weights for each primitive in the final active optimization space. Since the eigenvectors of $\mathbf{BB}^T$ form a complete, orthonormal set, the weight for each primitive in the *total* vector space (nonredundant and redundant) must equal unity. As can be seen from the actual weights, all the stretches are needed to describe motions in fluoroethylene, but only two thirds, so to say, of each bend are required; one third of each bend is redundant. All of the torsions have been eliminated (mainly due to symmetry).

Let us now take a closer look at the coordinates (the eigenvectors of $\mathbf{BB}^T$) themselves. What is it about the particular linear combination of primitives that make a given internal coordinate redundant? Examination of the first redundant coordinate for fluoroethylene shows that this comprises a constant ($-0.567\,186$) times the sum of the three angles around one of the carbon atoms plus another constant ($0.107\,858$) times the sum of the angles around the other carbon atom. Since fluoroethylene is planar, the sum of the three angles around each of the carbon atoms is always 2π. In other words, this coordinate is always constant no matter what the geometry of (planar) fluoroethylene is. A coordinate which always has the same fixed value is obviously no use at all for describing geometrical changes. It is clearly redundant. Examination of the two other redundant coordinates shows exactly the same thing; these two coordinates also never change.

This appears to be a general conclusion, and we can state

```
   SCHEME 1
   --------

   DELOCALIZED INTERNAL COORDINATES AS GENERATED FOR FLUOROETHYLENE


          Z-Matrix  (Angstroms and Degrees)

   1  C
   2  C           1   1.400000
   3  F           1   1.400000    2   118.0000
   4  H           1   1.000000    2   120.0000    3   180.0000
   5  H           2   1.000000    1   120.0000    3   180.0000
   6  H           2   1.000000    1   120.0000    5   180.0000

    Cartesian Coordinates in Standard Orientation

                      Coordinates (Angstroms)
    ATOM              X           Y           Z
   1  C           -.061684     .673790     .000000
   2  C           -.061684    -.726210     .000000
   3  F           1.174443    1.331050     .000000
   4  H           -.927709    1.173790     .000000
   5  H           -.927709   -1.226210     .000000
   6  H            .804342   -1.226210     .000000
  Point Group: cs    Number of degrees of freedom:   9


Attempting to Generate Delocalized Internal Coordinates
Generating Primitive Internal Coordinates
Primitive Stretches:
        2    1
        3    1
        4    1
        5    2
        6    2
There are      5 Stretches
Primitive Bends:
        2    1    3
        2    1    4
        3    1    4
        5    2    1
        6    2    1
        5    2    6
There are      6 Bends
Primitive Torsions:
        5    2    1    3
        5    2    1    4
        6    2    1    3
        6    2    1    4
There are      4 Torsions
There are     15 Primitive Internals

Generating Delocalized Internal Coordinates

  Eigenvalues of B*B(t):
     .000000     .000000     .000000     .252815     .401636     .629534
     .891612     .955159    1.155581    2.022821    2.371730    2.616216
    3.976390    4.205934    4.712469
   Eigenvectors:


        .000000     .000000     .000000     .175107    -.697853     .128293
        .000000     .000000     .000000     .113495    -.084799    -.224090
        .000000     .000000     .000000    -.113417    -.128883     .389279
        .000000     .000000     .000000    -.015690    -.185081    -.330747
        .000000     .000000     .000000     .077121    -.062552     .372297
       -.567186     .000000    -.107858     .625063    -.071762    -.324313
       -.567186     .000000    -.107858    -.418705    -.304491     .270802
       -.567186     .000000    -.107858    -.206358     .376253     .053511
        .107858     .000000    -.567186    -.364868    -.338833    -.382234
        .107858     .000000    -.567186     .436506     .029079     .449242
        .107858     .000000    -.567186    -.071638     .309754    -.067008
        .000000     .500000     .000000     .000000     .000000     .000000
        .000000    -.500000     .000000     .000000     .000000     .000000
        .000000    -.500000     .000000     .000000     .000000     .000000
        .000000     .500000     .000000     .000000     .000000     .000000


        .132483    -.064087     .000000     .000000     .127604     .004490
        .650512    -.087705     .000000     .000000    -.155555    -.547092
        .471004    -.081050     .000000     .000000    -.536536     .388010
        .015454    -.597404     .000000     .000000     .159544     .547045
       -.080323    -.593763     .000000     .000000     .337296    -.399602
       -.126727     .006642     .000000     .000000    -.221506     .017963
       -.312650     .014344     .000000     .000000    -.212676    -.162313
        .439377    -.020987     .000000     .000000     .434182     .144350
        .077057     .212457     .000000     .000000     .196273    -.040960
        .048011     .212980     .000000     .000000     .211566     .163933
       -.125068    -.425438     .000000     .000000    -.407839    -.122973
        .000000     .000000    -.728579     .442261     .000000     .000000
        .000000     .000000    -.341123    -.258123     .000000     .000000
        .000000     .000000    -.566385    -.146047     .000000     .000000
        .000000     .000000    -.178929    -.846432     .000000     .000000


        .559070     .339644     .000000
        .039006    -.416923     .000000
       -.336300     .197618     .000000
       -.009626    -.417337     .000000
       -.426972     .191762     .000000
       -.248647     .195749     .000000
        .052171    -.391216     .000000
        .196475     .195467     .000000
       -.378219     .195705     .000000
       -.001546    -.392636     .000000
        .379765     .196931     .000000
        .000000     .000000    -.153550
        .000000     .000000    -.752999
        .000000     .000000     .638653
        .000000     .000000     .039204

 There are      3 Redundant primitive internals
 Eliminated     3 Coordinates due to Symmetry
```

Scheme 1. (*Continued.*)



```
 Final Set of Active Internal Coordinates


     .175107    -.697853     .128293     .132483    -.064087     .127604
     .113495    -.084799    -.224090     .650512    -.087705    -.155555
    -.113417    -.128883     .389279     .471004    -.081050    -.536536
    -.015690    -.185081    -.330747     .015454    -.597404     .159544
     .077121    -.062552     .372297    -.080323    -.593763     .337296
     .625063    -.071762    -.324313    -.126727     .006642    -.221506
    -.418705    -.304491     .270802    -.312650     .014344    -.212676
    -.206358     .376253     .053511     .439377    -.020987     .434182
    -.364868    -.338833    -.382234     .077057     .212457     .196273
     .436506     .029079     .449242     .048011     .212980     .211566
    -.071638     .309754    -.067008    -.125068    -.425438    -.407839
     .000000     .000000     .000000     .000000     .000000     .000000
     .000000     .000000     .000000     .000000     .000000     .000000
     .000000     .000000     .000000     .000000     .000000     .000000
     .000000     .000000     .000000     .000000     .000000     .000000


     .004490     .559070     .339644
    -.547092     .039006    -.416923
     .388010    -.336300     .197618
     .547045    -.009626    -.417337
    -.399602    -.426972     .191762
     .017963    -.248647     .195749
    -.162313     .052171    -.391216
     .144350     .196475     .195467
    -.040960    -.378219     .195705
     .163933    -.001546    -.392636
    -.122973     .379765     .196931
     .000000     .000000     .000000
     .000000     .000000     .000000
     .000000     .000000     .000000
     .000000     .000000     .000000

Primitive Weights in Final Active Optimization Space

Weight for primitive     1 is    1.000000
Weight for primitive     2 is    1.000000
Weight for primitive     3 is    1.000000
Weight for primitive     4 is    1.000000
Weight for primitive     5 is    1.000000
Weight for primitive     6 is     .666667
Weight for primitive     7 is     .666667
Weight for primitive     8 is     .666667
Weight for primitive     9 is     .666667
Weight for primitive    10 is     .666667
Weight for primitive    11 is     .666667
Weight for primitive    12 is     .000000
Weight for primitive    13 is     .000000
Weight for primitive    14 is     .000000
Weight for primitive    15 is     .000000
```

Scheme 1. (*Continued.*)

that internal coordinates classified as redundant by forming and diagonalizing the $\mathbf{BB}^T$ matrix are redundant because they are constant and are not affected by any geometrical changes in the molecule. In the sense that the redundant subspace is completely constant, then the nonredundant (active) subspace must be ‘‘completely active,’’ i.e., because the redundant subspace contains nothing of any use at all for describing geometrical changes, then all the ‘‘good stuff’’ must be in the nonredundant subspace, and in this sense we claim that the set of nonredundant internal coordinates generated form the $\mathbf{BB}^T$ matrix is initially the ‘‘best’’ set possible. (In fact, what one should really say is that the nonredundant vector *subspace* generated is the ‘‘best’’ possible, rather than the specific coordinates—see later.)

Actually, we have been somewhat disingenuous in choosing fluoroethylene as our example. In fluoroethylene the redundant coordinates are truly constant as can be clearly seen by inspection. However, strictly speaking, this will not be true in general. This is because the transformation from Cartesian to internal coordinates is nonlinear; the B matrix merely ‘‘linearizes’’ this transformation and can only be used for very small displacements. What we can say is that the redundant coordinates are constant in a *linearized sense*.

Having obtained our set of active internal coordinates (the vectors in $\mathbf{U}$ as defined above), the B matrix—which was constructed from the original primitive internals—is transformed to our active coordinate set according to

$$\mathbf{B}=\mathbf{U}^T\mathbf{B}^{\mathrm{prim}}. \tag{3}$$

Note that $\mathbf{B}^{\mathrm{prim}}$ denotes the *original* B matrix over the set of primitive internals and $\mathbf{B}$ the B matrix over the set of active (delocalized) internal coordinates.

We then construct the ‘‘inverse B matrix’’ in the normal manner.

$$(\mathbf{B}^T)^{-1}=(\mathbf{BB}^T)^{-1}\mathbf{B}, \tag{4}$$

and transform the gradient vector $\mathbf{g}$ (and Hessian matrix $\mathbf{H}$ if appropriate) from Cartesian to internal coordinates according to

$$\mathbf{g}=(\mathbf{B}^T)^{-1}\mathbf{g}^{\mathrm{cart}}, \tag{5a}$$

$$\mathbf{H}^{\mathrm{int}}=(\mathbf{B}^T)^{-1}(\mathbf{H}^{\mathrm{cart}}-\mathbf{g}^{\mathrm{int}}d\mathbf{B}/d\mathbf{X}^{\mathrm{cart}})[(\mathbf{B}^T)^{-1}]^T. \tag{5b}$$

Although the derivative of the B matrix (in Cartesian coordinates) is required for the *full* Hessian transformation in Eq. (5b), it is often advantageous to leave this term out, especially when using a Cartesian molecular mechanics Hessian calculated at a forcefield equilibrium geometry as a starting guess. This is because inclusion of the $\mathbf{g}^{\mathrm{int}}d\mathbf{B}/d\mathbf{X}^{\mathrm{cart}}$ term often changes the Hessian eigenvalue structure,[4,11] and it is clearly advantageous to start off a minimization, say, with a (known) positive definite Hessian. Large systems in particular, which may be some way off their final converged geometry, often give rise to Hessian matrices in internal coordinates with several (usually small) negative eigenvalues if this term is not omitted, which impede convergence. When using an equilibrium mechanics geometry as a starting guess, the $\mathbf{g}^{\mathrm{int}}d\mathbf{B}/d\mathbf{X}^{\mathrm{cart}}$ term should be left out in any case, since the corresponding mechanics gradient is zero. In many practical optimizations, the Hessian is approximated directly in internal coordinates on the first cycle and is thereafter updated, so the transformation from Cartesians is never actually done.

With all quantities transformed to internal coordinates, the actual optimization step can be determined using standard techniques[12,13] in the active internal coordinate space.

The final step is to transform the new geometry in internal coordinates back into Cartesians in order to calculate a new energy and gradient for the next optimization cycle. Since the transformation from Cartesians to internals is nonlinear, the same B matrix that was used at the start of the cycle to transform the old geometry cannot be used to transform the new. Instead this is done iteratively using the formula

$$\mathbf{X}^{\mathrm{cart}}(k+1)=\mathbf{X}^{\mathrm{cart}}(k)+[(\mathbf{B}^T)^{-1}]^T(k)[\mathbf{X}^{\mathrm{int}}-\mathbf{X}^{\mathrm{int}}(k)]. \tag{6}$$

Here $\mathbf{X}^{\mathrm{int}}$ is the (known) new geometry in internal coordinates and the iterative procedure is started $(k=1)$ by using the *old* Cartesian geometry (and the old B matrix). The procedure is terminated when the internal coordinates $\mathbf{X}^{\mathrm{int}}(k)$ generated on the kth iteration from the Cartesian set $\mathbf{X}^{\mathrm{cart}}(k)$ is identical to $\mathbf{X}^{\mathrm{int}}$ within a given tolerance. This iterative back-transformation normally converges extremely rapidly, and differences in $\mathbf{X}^{\mathrm{int}}-\mathbf{X}^{\mathrm{int}}(k)$ of $<10^{-10}$ can typically be achieved in only 3 or 4 cycles.

How do the nonredundant internal coordinates we have generated for fluoroethylene perform in practice, i.e., in an actual geometry optimization? Before answering that question, let us examine the natural internal coordinate set produced for fluoroethylene by a standard ‘‘direct examination’’ algorithm (we use the one in TURBOMOLE[9]). In this ‘‘traditional’’ scheme, stretches are always taken as coordinates in their own right and torsions will be discarded due to symmetry, so we only need to consider the bends. Using idealized local symmetry and the nomenclature for the bends as in Scheme 1, the following linear combinations are generated:

$$\begin{gathered}\frac{1}{\sqrt{6}}(2\angle_{213}-\angle_{214}-\angle_{314}),\\ \frac{1}{\sqrt{2}}(\angle_{214}-\angle_{314}),\\ \frac{1}{\sqrt{6}}(2\angle_{521}-\angle_{621}-\angle_{526}),\\ \frac{1}{\sqrt{2}}(\angle_{621}-\angle_{526}).\end{gathered} \tag{7}$$

Looking at the weight of the primitive bends in the above coordinates we see that in each case this is two thirds, exactly the same as the weights in our delocalized internal coordinates (Scheme 1). Given that all the stretches are included, we see that the two sets of internal coordinates span *the same active subspace*. Since two coordinate systems which are related by a linear transformation are equivalent in all gradient optimization methods if the gradient vector and the Hessian are properly transformed (as has been explicitly pointed out by Pulay and Fogarasi[6]), then the two sets of internal coordinates will perform *identically* in a given geometry optimization (provided they are given the same initial Hessian data).

For many small molecules, natural internal coordinates generated by ''direct examination'' algorithms and those generated by diagonalizing $\mathbf{BB}^T$ span *identical* subspaces and hence will perform identically in geometry optimizations. As the molecules become larger and more complex, this will no longer be true, but we would expect a fairly large overlap between the two coordinate spaces. In any case, we have already presented arguments that our delocalized internal coordinate space is initially the ''best'' one; we have also mentioned other advantages of the $\mathbf{BB}^T$ scheme.

The above analysis gives us complete confidence that internal coordinates obtained by diagonalizing the $\mathbf{BB}^T$ matrix, however complicated they may look, will perform in practice as well as, if not better than, any other set of nonredundant coordinates generated from the same set of initial primitives.

Note that, as the optimization progresses, then, in general, the nonredundant internal coordinate subspace, which was the ''best'' choice at the starting geometry, will no longer be optimal. It can be made so by reforming and rediagonalizing $\mathbf{BB}^T$ at each optimization cycle, effectively generating a new set of nonredundant internal coordinates at each step. In essence, this is what Pulay and Fogarasi are doing in their redundant optimization scheme.[6] However, in our experience, this has almost no effect on the overall performance as the subspace has to be very far from optimal for any effect to be noticeable. Indeed, if the effect were marked then the natural internal coordinate algorithms in current use would not perform as well as they do.

An optimal nonredundant subspace becomes ''nonoptimal'' by mixing in some of the redundant subspace (and vice versa). The effect of this mixing—which occurs naturally during the course of an optimization if the nonredundant subspace is not continually regenerated—can be investigated by deliberating mixing the two spaces at the start of the optimization. We have done this for fluoroethylene by replacing the lowest vector in the nonredundant subspace (corresponding to an eigenvalue of $\mathbf{BB}^T$ of 0.252 815, see Scheme 1) with a linear combination of itself and the ''highest'' vector in the redundant subspace. Even with 80% of this vector replaced by the redundant vector, there was no deterioration in performance (as measured by the number of optimization cycles required to reach convergence). With 90% replaced there was a marked deterioration; steps taken—when converted back to Cartesian space—were obviously inappropriate, and there were severe convergence problems with the iterative back-transformation.

What *does* impact the natural internal coordinate optimization is the behavior of the underlying primitive internals. In particular, if these become inappropriate to describe the molecular geometry then the optimization usually fails as a result of the failure of the back-transformation from internal coordinates to a new set of Cartesians. The principal culprits here are bond angles which, during the course of the optimization, become near-linear. This is a well known problem which is handled in a Z matrix (at least in its initial construction) by replacing bond angles near 180° by two angles to a suitably placed dummy atom of near 90°.

We handle this situation in our algorithm by monitoring the values of the primitive internals and if any bond angle seems to be heading towards 180° we replace the planar bend by linear coplanar and perpendicular bends and modify the torsions accordingly. A new set of delocalized internals is then generated, based on the revised set of primitives. The situation can work in reverse and linear bends can be replaced by planar bends plus additional torsions if necessary. Full details will be given elsewhere; suffice it to say that the method works well and essentially eliminates the last major obstacle to carrying out complete optimizations in ''natural'' internals under almost all foreseeable circumstances.

Before leaving this section, we would like to emphasize some of the advantages of our delocalized internal coordinates over the redundant internal coordinate scheme of Pulay and Fogarasi.[6] (The advantages with respect to standard natural internal coordinates have already been pointed out.)

Both our scheme and Pulay and Fogarasi's[6] start by forming and diagonalizing $\mathbf{BB}^T$ (although the underlying internal coordinates are different, being primitive and natural internal coordinates, respectively). However, we—in general—only ever do this *once* (after which our nonredundant coordinate subspace $\mathbf{U}$ never changes), whereas Pulay and Fogarasi do this at the beginning of *every* optimization cycle. Additionally—and actually more time consuming—the $\mathbf{BB}^T$ matrix has to be constructed and diagonalized in order to form the generalized inverse at *each* step of the iterative back-transformation in redundant internal coordinates, whereas we can form the matrix inverse in Eq. (6) by more efficient techniques (such as LU decomposition[14]).

Note that—as pointed out by Pulay and Fogarasi[6]—the generalized inverse can be constructed by singular value decomposition,[14] thus avoiding the matrix diagonalization. However, the redundant internal coordinate scheme requires additional transformations, and in carrying the *full* vector space (both redundant and nonredundant), it works with a space of higher dimension than the nonredundant subspace alone. (It may be of *much* higher dimension, depending on how the initial internal coordinate space is constructed.)

Although the extra transformations and higher dimension of the redundant internal coordinate scheme are of no real consequence in *ab initio* optimizations, they can have a significant impact on optimizations of large molecules using semiempirical or empirical (molecular mechanics) approaches which are orders of magnitude faster than *ab initio* computations. In such cases, the large dimension of the matrices involved results in a significant part of the total CPU time being spent in transformations to and from internal coordinates which may well offset the reduction in the number of cycles to reach convergence with respect to Cartesian coordinates. Our nonredundant delocalized internal coordinate scheme can be much more efficient under these circumstances.

B. Geometrical constraints

One advantage *Z*-matrix coordinates have long enjoyed over all other coordinate systems, is the relative ease with which standard geometrical constraints, i.e., fixed bond lengths, fixed bond angles, and fixed dihedral angles, can be applied. Bond length constraints are straightforward to apply with ''standard'' natural internal coordinates, as each bond length forms a single coordinate, but angle and torsion constraints are more problematic. With the internal coordinates proposed here, which are potentially linear combinations of *all* coordinates in the primitive space, it does not seem particularly straightforward to impose any constraints at all.

In fact, *all* standard constraints can be imposed by a relatively simple Schmidt-orthogonalization procedure. What is done is to take a unit vector with unit component corresponding to the primitive internal (stretch, bend, or torsion) that one wishes to keep constant. This vector is then projected onto the full active subspace, normalized, and then all (n, say) active vectors are Schmidt orthogonalized in turn to this normalized, projected constraint vector. The last vector taken in the active space should drop out (since it will be linearly dependent on the other vectors and the constraint vector) leaving $(n-1)$ active vectors and one constraint vector.

In more detail, the procedure is as follows. The initial (usually unit) constraint vector $\mathbf{C}$ is projected onto the active subspace according to

$$\mathbf{C}^{\text{proj}}=\Sigma\langle\mathbf{C}|\mathbf{U}_k\rangle\mathbf{U}_k, \tag{8}$$

where the summation is over all n active vectors $\mathbf{U}_k$. The projected vector $\mathbf{C}^{\text{proj}}$ is then normalized and an $(n+1)$ dimension vector space $\mathbf{V}$ is formed, comprising the normalized, projected constraint vector together with all vectors in the active space

$$\mathbf{V}=\{\mathbf{C}^{\text{proj}},\mathbf{U}_k \quad k=1\cdots n\}. \tag{9}$$

This set of vectors is Schmidt orthogonalized according to the standard recipe

$$\tilde{\mathbf{V}}_k=\alpha_k\Big(\mathbf{V}_k-\sum_{l=1}^{k-1}\langle\mathbf{V}_k|\tilde{\mathbf{V}}_l\rangle\tilde{\mathbf{V}}_l\Big), \tag{10}$$

where the first vector taken, $\mathbf{V}_1$ is $\mathbf{C}^{\text{proj}}$. The α_k in Eq. (10) is a normalization factor. As noted above, the last vector taken, $\mathbf{V}_{n+1}=\mathbf{U}_n$, will drop out, leaving a fully orthonormal set of $(n-1)$ active vectors and one constraint vector.

After the Schmidt orthogonalization the constraint vector will contain *all* the weight in the active subspace of the primitive to be fixed, which will have a zero component in all of the other $(n-1)$ active vectors. The fixed primitive has thus been isolated entirely in the constraint vector which can now be removed from the active subspace for the geometry optimization step.

We illustrate this procedure below, again using fluoroethylene as our example. We consider a constrained optimization of fluoroethylene in which both the C–C bond length and the ∠HCF bond angle remain fixed.

The initial set of active delocalized internal coordinates generated for fluoroethylene have already been described, and are the final set shown in Scheme 1. The Schmidt-orthogonalization procedure is shown in Scheme 2. Projection of two initial unit vectors (with unit components in positions 1—corresponding to the C–C stretch—and 8—corresponding to the ∠HCF bend) using Eq. (8) give the two unnormalized projected vectors shown near the top of Scheme 2. These are then normalized to give the second set shown.

For the C–C bond, the final normalized constraint vector is a simple unit vector. This is because the C–C stretch has a full weight of unity in the initial active subspace. The constraint vector for the ∠HCF bond angle is *not* a unit vector, precisely because the weight for this bend is not unity in the initial subspace.

The Schmidt-orthogonalization procedure removes two internal coordinates from the active space, leaving seven active and two constraint vectors as shown. Also given are the primitive weights in the final active optimization space (which comprises the seven active vectors). The weight for the two primitives which are to remain fixed is of course zero.

Although the final set of internal coordinates looks very different from our initial set—the set used for the unconstrained optimization (Scheme 1)—if we include the two constraint vectors in the active space, then we will span exactly the same subspace as with the unconstrained set. Thus an *unconstrained* optimization of fluoroethylene using the set of nine internal coordinates shown in Scheme 1 and one using the $(7+2)$ internal coordinates shown in Scheme 2 will perform *identically*. (Note that, although the constraint vectors are eliminated from the active space during the actual optimization, they are needed for the iterative back-transformation from internals to Cartesians. For this purpose the *projected* constraint vector is replaced by the *original* unit vector from which it was derived.)

In addition to constraints on individual primitives, it is possible to impose combinatorial constraints. For example, if, instead of a unit vector, one started the constraint procedure with a vector in which *two* components were set to unity, then this would impose a constraint in which the *sum* of the two relevant primitives were always constant. Perhaps the ''ultimate'' such constraint would be to simply leave out one (or more) of the original internal coordinates; one would then be able to perform an optimization in which some complicated linear combination of potentially *all* the primitives would be kept constant.

We illustrate a combinatorial constraint by again considering fluoroethylene, and requesting that the sum of the ∠HCF and ∠HCH bond angles remain constant. These two bends correspond to primitives 8 and 11, respectively. The Schmidt-orthogonalization procedure is shown in Scheme 3. The initial vector—not shown—had unit entries in positions

```
  SCHEME 2
  --------

  IMPOSING CONSTRAINTS ON FLUOROETHYLENE BY SCHMIDT-ORTHOGONALIZATION


          Constraints and their Current Values
 number   coeff.     type      atoms involved       value
    1   1.000000   distance     2   1             1.400000
    2   1.000000      angle     3   1   4          122.000


Imposing Constraints by Schmidt Orthogonalization
 unnormalized projected vectors are


    1.000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000    -.333333
     .000000    -.333333
     .000000     .666667
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000

 normalized projected vectors are


    1.000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000    -.408248
     .000000    -.408248
     .000000     .816497
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000
     .000000     .000000

Eliminating Active Internal Coordinate     8
Eliminating Active Internal Coordinate     9
Number of Delocalized Internals Left in Active Space is     7
```

```
    Schmidt-Orthogonalized Set of   7 Active and   2 Constraint Vectors

      .000000     .000000     .000000     .000000     .000000     .000000
      .119273    -.235268    -.197601     .747085    -.096609     .557196
     -.119190    -.203015     .421631     .560497    -.099528    -.648064
     -.016488    -.371101    -.289832    -.170703    -.622043    -.248878
      .081047    -.169979     .401395    -.209070    -.618193     .333706
      .548452    -.043468    -.294129     .013958    -.003950    -.204981
     -.548452     .043468     .294129    -.013958     .003950     .204981
      .000000     .000000     .000000     .000000     .000000     .000000
     -.383443    -.497673    -.328501    -.092934     .186116    -.015445
      .458728    -.176328     .482973    -.097603     .189493     .084707
     -.075285     .674001    -.154472     .190537    -.375609    -.069262
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000


      .000000    1.000000     .000000
      .115928     .000000     .000000
     -.150851     .000000     .000000
      .547716     .000000     .000000
     -.515934     .000000     .000000
     -.261861     .000000    -.408248
      .261861     .000000    -.408248
      .000000     .000000     .816497
     -.347179     .000000     .000000
      .373192     .000000     .000000
     -.026013     .000000     .000000
      .000000     .000000     .000000
      .000000     .000000     .000000
      .000000     .000000     .000000
      .000000     .000000     .000000


 Primitive Weights in Final Active Optimization Space

 Weight for primitive     1 is      .000000
 Weight for primitive     2 is     1.000000
 Weight for primitive     3 is     1.000000
 Weight for primitive     4 is     1.000000
 Weight for primitive     5 is     1.000000
 Weight for primitive     6 is      .500000
 Weight for primitive     7 is      .500000
 Weight for primitive     8 is      .000000
 Weight for primitive     9 is      .666667
 Weight for primitive    10 is      .666667
 Weight for primitive    11 is      .666667
 Weight for primitive    12 is      .000000
 Weight for primitive    13 is      .000000
 Weight for primitive    14 is      .000000
 Weight for primitive    15 is      .000000
```

Scheme 2. (*Continued.*)

```
  SCHEME 3
  --------

  NON-STANDARD "COMBINATORIAL" CONSTRAINT IMPOSED ON FLUOROETHYLENE


           Constraints and their Current Values
 number   coeff.     type      atoms involved       value
    1   1.000000      angle     3   1   4          122.000
        1.000000      angle     5   2   6          120.000


Imposing Constraints by Schmidt Orthogonalization
 unnormalized projected vectors are


      .000000
      .000000
      .000000
      .000000
      .000000
     -.333333
     -.333333
      .666667
     -.333333
     -.333333
      .666667
      .000000
      .000000
      .000000
      .000000

 normalized projected vectors are


      .000000
      .000000
      .000000
      .000000
      .000000
     -.288675
     -.288675
      .577350
     -.288675
     -.288675
      .577350
      .000000
      .000000
      .000000
      .000000

Eliminating Active Internal Coordinate     9
Number of Delocalized Internals Left in Active Space is     8
```

```
  Schmidt-Orthogonalized Set of     8 Active and     1 Constraint Vectors


      .180413    -.916110     .137371    -.084826     .300254     .102864
      .116935    -.129026    -.222574     .658632    -.195017    -.147175
     -.116854    -.141206     .390302     .477155    -.162522    -.530312
     -.016165    -.231036    -.328679    -.034046    -.621696     .167959
      .079458    -.093909     .373446    -.115608    -.631781     .346760
      .572400     .019460    -.326247    -.086430    -.049923    -.217772
     -.502999    -.074440     .266694    -.232850    -.090216    -.205657
     -.069401     .054980     .059553     .319280     .140139     .423429
     -.447530    -.128204    -.385756     .171237     .073333     .203819
      .378129     .183184     .445308     .148044     .066806     .219610
      .069401    -.054980    -.059553    -.319280    -.140139    -.423429
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000


     -.015534     .033940     .000000
     -.540631     .366566     .000000
      .392938    -.352631     .000000
      .554231     .339535     .000000
     -.391906    -.398825     .000000
      .020876    -.301749    -.288675
     -.156809     .352727    -.288675
      .135933    -.050978     .577350
     -.034735    -.374643    -.288675
      .170668     .323666    -.288675
     -.135933     .050978     .577350
      .000000     .000000     .000000
      .000000     .000000     .000000
      .000000     .000000     .000000
      .000000     .000000     .000000


 Primitive Weights in Final Active Optimization Space

 Weight for primitive     1 is    1.000000
 Weight for primitive     2 is    1.000000
 Weight for primitive     3 is    1.000000
 Weight for primitive     4 is    1.000000
 Weight for primitive     5 is    1.000000
 Weight for primitive     6 is     .583333
 Weight for primitive     7 is     .583333
 Weight for primitive     8 is     .333333
 Weight for primitive     9 is     .583333
 Weight for primitive    10 is     .583333
 Weight for primitive    11 is     .333333
 Weight for primitive    12 is     .000000
 Weight for primitive    13 is     .000000
 Weight for primitive    14 is     .000000
 Weight for primitive    15 is     .000000
```

Scheme 3. (*Continued.*)

```
    SCHEME 4
    --------

    LOCALIZED INTERNAL COORDINATES AS GENERATED FOR FLUOROETHYLENE


 Localizing Internal Coordinates by Schmidt Orthogonalization

 Eliminating Primitive    12  This has a Zero Projected Vector
 Eliminating Primitive    13  This has a Zero Projected Vector
 Eliminating Primitive    14  This has a Zero Projected Vector
 Eliminating Primitive    15  This has a Zero Projected Vector

 Normalized Projected Localized Vectors


     1.000000     .000000     .000000     .000000     .000000     .000000
      .000000    1.000000     .000000     .000000     .000000     .000000
      .000000     .000000    1.000000     .000000     .000000     .000000
      .000000     .000000     .000000    1.000000     .000000     .000000
      .000000     .000000     .000000     .000000    1.000000     .000000
      .000000     .000000     .000000     .000000     .000000     .816497
      .000000     .000000     .000000     .000000     .000000    -.408248
      .000000     .000000     .000000     .000000     .000000    -.408248
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000     .000000


      .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000
     -.408248    -.408248     .000000     .000000     .000000
      .816497    -.408248     .000000     .000000     .000000
     -.408248     .816497     .000000     .000000     .000000
      .000000     .000000     .816497    -.408248    -.408248
      .000000     .000000    -.408248     .816497    -.408248
      .000000     .000000    -.408248    -.408248     .816497
      .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000
      .000000     .000000     .000000     .000000     .000000
 Final Set of Localized Internal Coordinates


    1.000000     .000000     .000000     .000000     .000000     .000000
     .000000    1.000000     .000000     .000000     .000000     .000000
     .000000     .000000    1.000000     .000000     .000000     .000000
     .000000     .000000     .000000    1.000000     .000000     .000000
     .000000     .000000     .000000     .000000    1.000000     .000000
     .000000     .000000     .000000     .000000     .000000     .816497
     .000000     .000000     .000000     .000000     .000000    -.408248
     .000000     .000000     .000000     .000000     .000000    -.408248
     .000000     .000000     .000000     .000000     .000000     .000000
     .000000     .000000     .000000     .000000     .000000     .000000
     .000000     .000000     .000000     .000000     .000000     .000000
     .000000     .000000     .000000     .000000     .000000     .000000
     .000000     .000000     .000000     .000000     .000000     .000000
     .000000     .000000     .000000     .000000     .000000     .000000
     .000000     .000000     .000000     .000000     .000000     .000000


     .000000     .000000     .000000
     .000000     .000000     .000000
     .000000     .000000     .000000
     .000000     .000000     .000000
     .000000     .000000     .000000
     .000000     .000000     .000000
     .707107     .000000     .000000
    -.707107     .000000     .000000
     .000000     .816497     .000000
     .000000    -.408248     .707107
     .000000    -.408248    -.707107
     .000000     .000000     .000000
     .000000     .000000     .000000
     .000000     .000000     .000000
     .000000     .000000     .000000

  Primitive Weights in Final Non-Redundant Optimization Space

  Weight for primitive     1 is    1.000000
  Weight for primitive     2 is    1.000000
  Weight for primitive     3 is    1.000000
  Weight for primitive     4 is    1.000000
  Weight for primitive     5 is    1.000000
  Weight for primitive     6 is     .666667
  Weight for primitive     7 is     .666667
  Weight for primitive     8 is     .666667
  Weight for primitive     9 is     .666667
  Weight for primitive    10 is     .666667
  Weight for primitive    11 is     .666667
  Weight for primitive    12 is     .000000
  Weight for primitive    13 is     .000000
  Weight for primitive    14 is     .000000
  Weight for primitive    15 is     .000000
```

Scheme 4. (*Continued.*)

8 and 11. Once again the internal coordinates generated are different from both previous sets (Schemes 1 and 2) but, once again, if the constraint vector is included, they span the same subspace. Note that in every active vector in the final set of internal coordinates (Scheme 3), the coefficients for the ∠HCF bend—primitive 8—and the ∠HCH bend—primitive 11—are equal and opposite in sign. Thus, for each internal coordinate in the optimization, if the ∠HCF angle is *increased*, the ∠HCH angle is *decreased* by the same amount, and vice versa. This is precisely what is needed to maintain the constraint.

Note that imposed constraints are *not* confined to those primitive internals generated by our initial connectivity scheme. If we wish to constrain a distance, angle, or torsion between atoms that are not formally connected, then all we need to do is add that particular coordinate to our primitive set. It can then be isolated and constrained in exactly the same way as a formal connectivity constraint.

C. Initial guess Hessian

In the above sections, we have presented our set of delocalized internal coordinates and have argued that, within the limitations of the underlying set of primitive internals, the nonredundant vector subspace that is generated by forming and diagonalizing the $\mathbf{BB}^T$ matrix is the ''best'' possible. We have already noted that *any* set of internal coordinates that span a given vector subspace will perform *identically* in a geometry optimization provided that optimizations using the different coordinates are given the same Hessian information. If a molecular mechanics Hessian in *Cartesian* coordinates is available, which is transformed according to Eq. (5b), then *all* optimizations within the vector subspace will be equivalent. In this event, it does not matter at all which set of coordinates is taken, and the original set of delocalized internal coordinates will be just as good as any other set.

There *is* a problem, however, if you do not have a means of generating a reliable initial Hessian. Under these circumstances what is often done is to guess an initial diagonal Hessian directly in the coordinate space that is being used for the optimization. One method that is known to work well with standard natural internals is to give coordinates involving stretches, bends, and torsions different force constants; typical values being, e.g., 0.5, 0.2, and 0.1 a.u., respectively. This is easy to do because natural internal coordinates involve either stretches, bends, or torsions *alone*—the different primitive types are not mixed. Delocalized internals, on the other hand, are *very* mixed. How do we generate a suitable starting Hessian for these coordinates?

One way of generating a suitable initial guess Hessian is to *localize* the coordinates. If our delocalized internal coordinates were transformed so that they looked more like natural internals then the same type of diagonal guess could be made for them too. Localization is in fact fairly easy to accomplish by an extension of the same Schmidt-orthogonalization procedure used to impose constraints. Instead of projecting just those primitives, we which to constrain onto the active subspace, we project *all* primitives. This will give a set of n vectors (where n is the number of primitive internals) which can be suitably Schmidt orthogonalized among themselves to give a new set of active vectors which will be *localized*. For example, in almost all molecules, stretches have a weighting of unity or thereabouts in the active space, and so projecting m primitive stretches will give m unit, or almost unit, vectors, i.e., all the stretches have been isolated. A similar thing happens, although not so marked, for the bends and torsions.

We illustrate this localization procedure, again using fluoroethylene as our example, in Scheme 4. Projecting each primitive internal onto the final set of active vectors for fluoroethylene shown in Scheme 1 gives the 11 vectors shown at the beginning of Scheme 4 (the four torsions are eliminated as, with no weight in the active space, they have a zero projection vector). These vectors are not all independent, and Schmidt orthogonalization gives the final set of nine localized internal coordinates. These localized coordinates will, of course, span exactly the same active subspace as the initial set of delocalized internals.

In the case of fluoroethylene, we have now come full circle, as it were. Starting from the same underlying primitive internals, we first generated a set of delocalized internal coordinates that spanned the *same* subspace as standard natural internals; using the above localization procedure we have now generated precisely the *same* coordinates [see Scheme 4 and Eq. (7)].

Localization will not in general generate a set of coordinates as ''clean'' as those obtained for fluoroethylene. What will typically happen in large systems is that vectors will be dominated by a few primitives, but will have a fairly large number of small components for other primitives, i.e., they will have associated with them some ''noise.'' However, they will certainly be ''pure'' enough to be designated as stretch, bend, or torsion dominated and hence to generate an appropriate diagonal Hessian element.

After spending, relatively speaking, so much time on localized internal coordinates, it is almost a shame to have to say that the above discussion was provided essentially for pedagogical purposes only, namely to show how coordinates similar to the perhaps more familiar natural internals could be obtained from our set of delocalized internal coordinates. We do *not* use localized internal coordinates in an actual optimization.

The fact is that we can generate an appropriate (and very much related) initial guess Hessian by a far simpler procedure within our delocalized internal coordinate space. Instead of trying to designate each internal coordinate as either stretch, bend, or torsion (and assigning to it an appropriate diagonal Hessian element) we assign the force constant to each primitive *directly*. This is done by setting up a diagonal ''Hessian'' matrix, $\mathbf{H}^{\text{prim}}$, in the *primitive* space, with diagonal entries appropriate for each primitive type. This matrix is then transformed to our active optimization space according to

$$\mathbf{H}=\mathbf{U}^T\mathbf{H}^{\text{prim}}\mathbf{U}. \tag{11}$$

If $\mathbf{H}^{\text{prim}}$ were simply a unit matrix, this procedure would

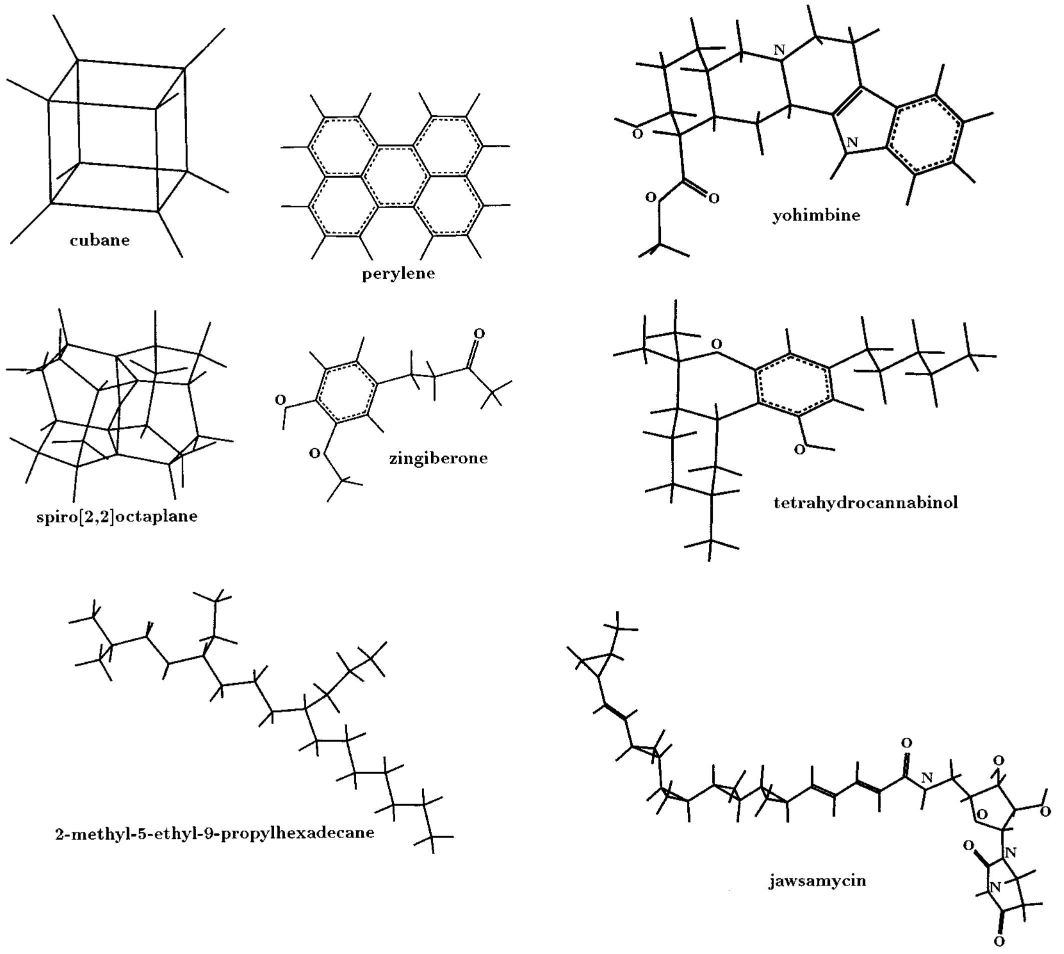


FIG. 1. Schematic diagram of the eight molecules in the test set for unconstrained optimization (see Table II and text).

result in a diagonal (unit) Hessian, **H**, in the active space. However, since $\mathbf{H}^{\mathrm{prim}}$ is not a unit matrix, the resulting active-space Hessian will *not* be diagonal. In this way we have mimicked the effect of having a diagonal Hessian in a localized internal coordinate space by using a nondiagonal Hessian in the delocalized internal coordinate space.

Although we could probably improve our initial Hessian guess, e.g., by using different primitive force constants depending on the bonding environment for each particular primitive in the actual molecule,[15] this simple Hessian guess performs very well in practice as the following examples will demonstrate.

III. EXAMPLES

A. Unconstrained optimizations

The delocalized internal coordinate scheme described above has been implemented in the OPTIMIZE program.[8] In this section, we present optimizations on a test set of eight fairly large (certainly by *ab initio* standards) systems, comparing the performance of delocalized internal coordinates with Cartesian coordinates and with standard natural internals. The eight molecules in our test set are : cubane (C_8H_8), perylene ($C_{20}H_{12}$), spiro[2,2]octaplane ($C_{21}H_{24}$), zingiberone ($C_{11}H_{14}O_3$), yohimbine ($C_{21}H_{26}N_2O_3$), tetrahydrocannabinol ($C_{21}H_{32}O_2$), 2-methyl-5-ethyl-9-propylhexadecane ($C_{22}H_{46}$), and jawsamycin ($C_{32}H_{43}N_3O_6$). Structures for these molecules are shown in Fig. 1.

Cubane was chosen as a cage compound with high symmetry (O_h). Perylene is planar (D_{2h} symmetry) with five benzene-like rings fused together. Spiro[2,2]octaplane is also a cage compound, but larger than cubane and with lower symmetry (D_2). Zingiberone is a (hot) component of ginger. 2-methyl-5-ethyl-9-propylhexadecane (henceforth denoted *R*-hexadecane) was selected at random as a relatively long chain hydrocarbon. The other three are large, unsymmetrical drug molecules with various (fused) rings and side chains. Yohimbine is reputedly an aphrodisiac. The antifungal drug ''jawsamycin'' was featured in a recent edition of *New Scientist*; its name derives from the chain of cyclopropyls which supposedly ''resemble the teeth of a shark.''[16]

Energies and gradients for the above systems were calculated using the standard defaults in the semiempirical package ZINDO[17] and were then fed into OPTIMIZE for the optimization step. Starting geometries for perylene, zingiberone, yohimbine, tetrahydrocannabinol, *R*-hexadecane, and jawsamycin were obtained by preoptimizing with the default mechanics forcefield in DISCOVER;[18] that for

TABLE I. Generation of delocalized internal coordinates. Number of primitive internals (stretches, bends, and torsions), number of redundant and nonredundant coordinates, and number of active coordinates in the final optimization space for the eight systems in the test set (see Fig. 1).

System	Formula	Sym	Primitives	Redundant	Nonredundant	Active
Cubane	C_8H_8	O_h	176	134	42	2
Perylene	$C_{20}H_{12}$	D_{2h}	192	102	90	16
Spiro[2,2]octaplane	$C_{21}H_{24}$	D_2	444	315	129	33
Zingiberone	$C_{11}H_{14}O_3$	C_1	133	55	78	78
Tetrahydrocannabinol	$C_{21}H_{32}O_2$	C_1	336	177	159	159
Yohimbine	$C_{21}H_{26}N_2O_3$	C_1	337	187	150	150
R-hexadecane	$C_{22}H_{46}$	C_1	388	190	198	198
Jawsamycin	$C_{32}H_{43}N_3O_6$	C_1	558	312	246	246

spiro[2,2]octaplane was kindly provided (as a *Z* matrix) by Danne Rasmussen (Australian National University). Cubane had initial C–C and C–H bond lengths of 1.5875 and 0.8249 Å, respectively. Molecular mechanics Hessians at the starting geometry were in all cases calculated using DISCOVER.

For each system, two optimizations were performed in each of the three coordinate systems, namely optimizations in either Cartesian, natural internal, or delocalized internal coordinates using either (1) a default starting Hessian or (2) the molecular mechanics Hessian. The default Hessian in Cartesians was a simple unit matrix; that in natural internals was a diagonal matrix with entries of 0.5 a.u. for stretches and 0.2 a.u. for all other coordinate types; and the starting Hessian in delocalized internals was generated as discussed in the Theory section above using Eq. (11). All optimizations were carried out with the standard EF algorithm,[12] utilizing a BFGS Hessian update,[19] and a maximum allowed step size (in internal or Cartesian space where appropriate) of 0.3 a.u. The convergence criteria used were an energy change from the previous cycle of less than 10^{-6} hartree and a maximum gradient component (in *Cartesian* coordinates for *all* optimizations, including those in internal coordinates) of magnitude less than 0.0003 a.u. When converting the (Cartesian) mechanics Hessian into internal coordinates, the gradient term involving the derivative of the *B* matrix was omitted as discussed under the transformation Eq. (5b).

The first task of the internal coordinate optimizations is to generate the active delocalized internal coordinates from the initial set of primitives and this was successfully accomplished with relative ease for all eight test molecules. Some details of the internal coordinate generation are provided in Table I, which shows the number of initial primitives, the number of redundant and nonredundant coordinates and the number of active coordinates (which is the same as the number of symmetry-independent degrees of freedom in the molecule). Note, that the number of nonredundant internals is typically less than half the number of initial primitives, indicating the amount of ''baggage'' that would have to be carried around if the optimizations were done in the full primitive space. For the cage compounds this fraction is even less due to the increased connectivity in these systems. Indeed, because of its very high symmetry, the number of active internal coordinates in cubane (just 2) is dramatically less that the initial number of primitives (176). (The principal reason for including cubane was in fact to test whether the algorithm could successfully handle the symmetry).

Results—in terms of the number of optimization cycles to reach convergence—are shown in Table II. The entries in Table II speak for themselves. For the larger systems in particular, the effect of using internal coordinates—either natural internals where possible or delocalized internals—as opposed to Cartesians is major. Note that the original ''direct examination'' natural internal coordinate code in OPTIMIZE was only able to generate a suitable set of natural internals for half the molecules in the test set.

For the first three systems—all of which are rigid or

TABLE II. Unconstrained optimization performance. Number of optimization cycles to reach convergence for minimization using Cartesian, delocalized internal and natural internal coordinates, starting with a default (def) or a molecular mechanics (mech) Hessian for the eight systems in the test set (see Fig. 1).

		Cartesians		Delocalized		Natural[a]	
System	Number of variables	def	mech	def	mech	def	mech
Cubane	2	7	8	9	8	*f*	*f*
Perylene	16	23	10	8	10	*f*	*f*
Spiro[2,2]octaplane	33	54	13	20	13	*f*	*f*
Zingiberone	78	88	29	18	26	17	25
Tetrahydrocannabinol	159	189	33	23	20	23	18
Yohimbine	150	258	110	45	25	33	23
R-hexadecane	198	246	89	35	18	26	18
Jawsamycin	246	642	409	60	71	*f*	*f*

[a] *f* denotes failure to generate an initial set of natural internal coordinates.

fairly so and have relatively high symmetry—there is no difference at all in performance between Cartesian optimizations with a starting mechanics Hessian and the corresponding optimization in delocalized internals. Cubane is so rigid, and has so few degrees of freedom, that a decent starting Hessian is not even needed. There is also very little difference for the first of the C_1 molecules, zingiberone (which, with 28 atoms, can be considered as ''medium sized''). However, apart from cubane, for these four systems Cartesian optimizations degrade significantly without a reliable starting Hessian. In delocalized internals, on the other hand, there is no marked difference in performance between optimizations with or without a ''good'' starting Hessian; in fact for perylene and zingiberone the performance is worse with the mechanics starting Hessian than with the default guess.

Results for the first four molecules in our test set are thus much as expected based on previous work[3]—Cartesian optimizations with a reliable starting Hessian are as good as the corresponding optimizations in internals; Cartesian optimizations without the initial Hessian information take typically 2–4 times as many cycles to converge as the corresponding internal coordinate optimization.

For the four larger, nonsymmetrical systems—yohimbine, tetrahydrocannabinol, *R*-hexadecane, and jawsamycin—the results are quite different. Here, even with a mechanics starting Hessian, the performance of the Cartesian optimization is *significantly* worse than the corresponding optimization in delocalized internals. The effect is not that marked with tetrahydrocannabinol, but for the other three molecules Cartesian optimizations with the mechanics Hessian take between 4 and 6 times *more* cycles to converge than the equivalent optimization in delocalized internals. With no initial Hessian information, Cartesian optimizations are worse by factors of up to 10.

Jawsamycin, with its long chain of three-membered cyclopropyl rings, is a nightmare for Cartesian coordinates. The rate of convergence (the speed of the energy decrease) in Cartesians is not that marked even at the start of the optimization, but towards the end progress is agonizingly slow, with energy changes of the order of 10^{-6} hartree per cycle. Not only does this result in incredibly slow convergence, but—since the energy change is so small—the final energy at convergence is higher than it should be as, once the gradient has converged, it only takes one cycle with a sub 10^{-6} hartree energy change to achieve convergence. Thus, the final ''converged'' structure has not actually converged to the same extent as the optimization in internal coordinates.

The situation for geometry optimization—assuming a ''reasonable'' starting structure—is thus as follows: (a) for small or very rigid medium-sized systems (say up to 15 or so atoms), optimizations in Cartesian and internal coordinates should perform similarly; (b) for medium-sized systems (say 15–30 atoms) optimizations in Cartesians should perform as well as optimizations in internal coordinates provided they are given a reliable starting Hessian; but (c) for large systems (30+ atoms)—unless these are fairly rigid—Cartesian coordinates simply cannot compete with a good set of internals, even with good quality Hessian information. As the system gets larger, with more long chains and less reliable starting geometries, the advantages of internal coordinates can only increase.

Comparing delocalized internal coordinates with standard natural internals for the four systems for which a set of natural internals could be generated, Table II shows that the performance is very similar when both optimizations use the mechanics starting Hessian. However, for two of the molecules—tetrahydrocannabinol and yohimbine—natural internals perform noticeably better with the default Hessian. We are convinced that this has nothing to do with either our default Hessian in delocalized internals or with the coordinates themselves, but is due solely to differences in the underlying set of primitive internals in the two optimizations.

The natural internal coordinate optimization generated its coordinates using the original ''direct examination'' algorithm in OPTIMIZE and, as a consequence, is much more ''selective'' in its choice of which primitives to use. An analysis of the 159 natural internal coordinates generated for yohimbine reveals that these used a total of 207 different primitive internals (56 stretches, 99 bends, 7 out-of-plane bends, and 45 torsions) compared to 337 different primitives for the delocalized internals (the same 56 stretches, 107 bends, and 174 torsions). Natural internal coordinates for yohimbine are thus constructed using far fewer torsions than for the construction of our set of delocalized internal coordinates; this is the result of our ''blanket'' approach to the underlying primitive space.

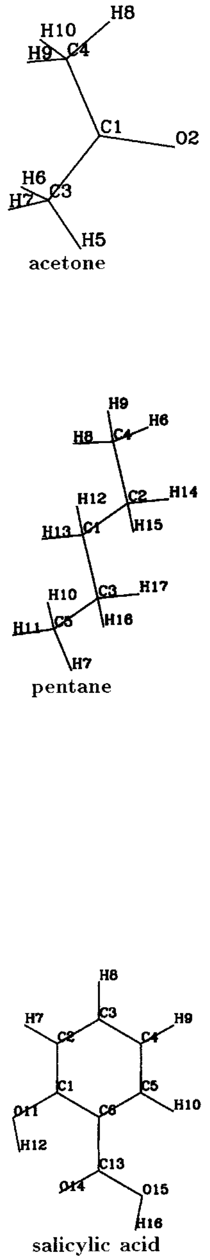
If the *same* set of primitives that were used for the construction of natural internals is used to generate delocalized internals, then optimization of yohimbine with the default Hessian takes just 27 cycles, i.e., 6 *fewer* than with the natural internal coordinate optimization. This supports our contention that we are generating the ''best'' coordinate set possible for the given primitive space.

Clearly, a more judicious choice of primitive internals could improve our optimization performance, and this is where we believe attention should be focused in the future. However, as the results in Table II demonstrate, we already have a highly successful, straightforward and—from the point of view of the user—*automatic* scheme for generating a set of internal coordinates suitable for geometry optimization for essentially *any* molecule.

B. Constrained optimizations

To demonstrate the utility of our constrained optimization procedure we present constrained optimizations on three fairly simple systems: acetone, pentane, and salicylic acid. These molecules, with full atom numbering, are shown in Fig. 2. The initial geometries were obtained from a *Z* matrix, and we directly compare constrained optimization in delocalized internal coordinates with the corresponding *Z*-matrix optimization. The starting *Z* matrices for each molecule (which are fairly well constructed) are also given in Fig. 2.

Details of the constraints imposed and the performance of the two coordinate systems (in terms of the number of cycles to reach convergence) are shown in Table III. We did



```
C1
O2  C1  L1                          L1 1.4
C3  C1  L2  O2  A1                  L2 1.56
C4  C1  L2  O2  A1  C3 180.0        L3 1.08
H5  C3  L3  C1  A2  O2   0.0        L4 1.08
H6  C3  L4  C1  A3  H5   D1         A1 120.0 *
H7  C3  L4  C1  A3  H5  -D1         A2 109.5
H8  C4  L3  C1  A2  O2   0.0        A3 109.5
H9  C4  L4  C1  A3  H8   D1         D1 120.0
H10 C4  L4  C1  A3  H8  -D1
```

```
C1
X1  C1  1.
C2  C1  L1  X1  A1
C3  C1  L1  X1  A1  C2  180.0     L1 1.60 *
X2  C2  1.  C1  A2  X1  180.0     L2 1.56
X3  C3  1.  C1  A2  X1  180.0     L3 1.08
C4  C2  L2  X2  A3  C1  180.0     L4 1.08
C5  C3  L2  X3  A3  C1  180.0     L5 1.08
H6  C4  L3  C2  A4  X2    0.0     L6 1.08
H9  C5  L3  C3  A4  X3    0.0     A1 120.0
H7  C4  L4  C2  A5  H6    D1      A2 120.0
H8  C4  L4  C2  A5  H6   -D1      A3 120.0
H10 C5  L4  C3  A5  H9    D1      A4 109.5
H11 C5  L4  C3  A5  H9   -D1      A5 109.5
H12 C1  L5  X1  A6  C2   90.0     A6  54.75
H13 C1  L5  X1  A6  C2  -90.0     A7  54.75
H14 C2  L6  X2  A7  C1   90.0     D1 120.0
H15 C2  L6  X2  A7  C1  -90.0
H16 C3  L6  X3  A7  C1   90.0
H17 C3  L6  X3  A7  C1  -90.0
```

```
                                    L1 1.20
                                    L2 0.70
                                    L3 1.40
                                    L4 1.20
                                    L5 0.70
X1                                  L6 0.70
X2  X1  L1                          L7 1.40
C1  X2  L2  X1 90.0                 L8 1.08
C2  X2  L2  X1 90.0 C1  180.0       L9 1.08
C3  X1  L3  X2 90.0 C1  180.0       L10 1.08
X3  X1  L4  C3 90.0 X2  180.0       L11 1.08
C4  X3  L5  X1 90.0 C3    0.0       L12 1.45
C5  X3  L6  X1  A1  C4  180.0       L13 1.00
C6  X1  L7  X2  A2  C3  180.0       L14 1.54
H7  C2  L8  C1  A3  C6  180.0       L16 1.45
H8  C3  L9  C2  A4  C1  180.0       L15 1.30 *
H9  C4  L10 C3  A5  C2  180.0       L17 1.00
H10 C5  L11 C4  A6  C3  180.0       A1   90.0
O11 C1  L12 C2  A7  C3  180.0       A2   90.0
H12 O11 L13 C1  A8  C2  180.0       A3   120.0
C13 C6  L14 C1  A9  C2  180.0       A4   120.0
O14 C13 L15 C6  A10 C5  180.0       A5   120.0
O15 C13 L16 C6  A11 C1  180.0       A6   120.0
H16 O15 L17 C13 A12 C6  180.0       A7   120.0
                                    A8   109.0 *
                                    A9   120.0
                                    A10 120.0
                                    A11 120.0
                                    A12 109.0
```

FIG. 2. Schematic diagram (with full atom numbering) of the three molecules used for constrained optimizations along with the initial Z matrix. The starred parameters in the Z matrix correspond to the coordinates that were fixed (see Table III and text).

two optimizations in each case, starting with (1) a unit Hessian; and (2) a default Hessian. In delocalized internals the default Hessian was the same as that used for the unconstrained optimizations [as obtained from Eq. (11)]; the default Z-matrix Hessian was diagonal with entries of 0.5 a.u. for stretches and 0.2 a.u. for bends and torsions. Additionally we carried out unconstrained optimizations on each system for comparison. Convergence criteria for all constrained optimizations were the same as for the unconstrained case, except that the gradient convergence criterion was with respect to the gradient in *internal* coordinates for obvious reasons.

TABLE III. Constrained optimization performance. Number of optimization cycles to reach convergence for constrained minimization using Z-matrix and Schmidt-orthogonalized delocalized internal coordinates, starting with a default or a unit Hessian for the three molecules in Fig. 2 (see text for more details).

	Z matrix		Delocalized	
System	unit	def	unit	def
Acetone				
Unconstrained	9	16	12	8
$aO_2C_1C_3$	8	14	12	8
$aO_2C_1C_3+rH_5H_8$[a]	⋯	⋯	13	7
Pentane				
Unconstrained	10	24	15	8
rC_1C_2	11	24	14	7
Salicylic acid				
Unconstrained	26	22	14	17
$aH_{12}O_{11}C_1+rC_{13}O_{14}$	25	27	14	17

[a] Nonconnectivity constraint (see text).

As can be seen from Table III, imposing constraints via Schmidt-orthogonalized delocalized internals is at least as efficient as with a Z matrix. Note, that the performance of the Z-matrix optimization with the default diagonal Hessian for both acetone and pentane is significantly worse than with a unit Hessian, even though the same type of Hessian works very well in natural internals. This is a result of the strong coupling between the different coordinates that is often present in a Z matrix, making a diagonal Hessian often a very poor starting guess. It is worth noting that energies at convergence were identical between the two coordinate systems to at least six decimal places.

In addition to the straightforward ''connectivity'' constraints, we illustrate the power of our Schmidt-orthogonalization approach by imposing an additional distance constraint in acetone between two of the methyl hydrogens (atoms 5 and 8; see Fig. 2) that are not formally connected. As shown in Table III, the corresponding constrained optimization is just as efficient as that for the simple angle constraint that was imposed.

Now it is of course possible to impose these ''nonconnectivity'' constraints in Z-matrix coordinates, but this would require construction of a nonstandard Z matrix, in which the constraint was one of the coordinates. If it were desired to impose a number of such constraints on a particular system, this would probably require writing a different Z matrix for each one. All such constraints can be imposed in a straightforward manner within our Schmidt-orthogonalization scheme.

We have imposed a number of such constraints on the larger molecules considered in our test set for unconstrained optimization (for none of which are we particularly keen to construct a Z matrix), and all constrained optimizations converged with no problems at all. The technique is clearly very powerfully and widely applicable.

IV. SUMMARY

Following the earlier work of Pulay and Fogarasi[6] we have presented a set of *delocalized internal coordinates* suitable for use in geometry optimizations. These coordinates are an alternative to standard natural internals, over which they have a number of advantages:

(1) They are much simpler to generate than natural internals, which are formed by ''direct examination'' of the molecular topology and which require several thousand lines of code to deal with the various structural possibilities.

(2) They can be generated for *any* molecular topology, unlike ''direct examination'' algorithms which often have difficulty generating suitable coordinates for cage compounds or multiply fused rings.

(3) They form a fully nonredundant coordinate set, whereas most algorithms for generating natural internals often produce more coordinates than are required to characterize the relative positions of the nuclei.

(4) By a suitable Schmidt-orthogonalization procedure *any* distance, angle or torsion constraint, or any linear combination thereof, can be imposed between *any* atoms in the molecule, including constraints between atoms that are not formally bonded. Imposed constraints are satisfied exactly.

ACKNOWLEDGMENTS

One of us (J.B.) would like to acknowledge the directors and staff of the Paul Scherrer Institut, Zurich for inviting him to the institute as a guest scientist. Particular thanks go to Dr. B. Patterson and Dr. K. Knop. This work was started and completed within a three month period from November 1995–January 1996.

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