An Algorithm for the Location of Transition States

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An algorithm for locating transition states designed for use in the *ab initio* program package GAUS-SIAN 82 is presented. It is capable of locating transition states even if started in the wrong region of the energy surface, and, by incorporating the ideas on hessian mode following due to Cerjan and Miller, can locate transition states for alternative rearrangement/dissociation reactions from the same initial starting point. It can also be used to locate minima.

INTRODUCTION

There has been considerable attention in recent years to improved methods of geometry optimization, i.e., the location of stationary points corresponding to minima and transition states on potential energy surfaces. The widespread availability of efficient computational algorithms to obtain analytical gradients for a large range of *ab initio* wave functions,[1-4] and even analytical second-derivatives in certain cases,[3,5] has greatly assisted in the search for reliable and efficient algorithms to locate stationary points.

Of particular note in this regard is the well known *ab initio* program package GAUS-SIAN 82,[6] which incorporates very good gradient routines and an efficient minimization algorithm, mainly due to Schlegel.[7] Although normally very successful at locating minima, this algorithm leaves a lot to be desired when it comes to the location of transition states.

Transition states are characterized as stationary points having one, and only one, negative hessian eigenvalue (the hessian being the matrix of second energy derivatives with respect to the geometrical parameters being varied). Minima have all positive hessian eigenvalues. The requirement of a negative hessian eigenvalue means that one has to be much more careful as regards the type of step taken on the energy surface when searching for a transition state than for a minimum. For example, if all else fails, it is always possible to take the steepest descent step in a minimum search, which is "guaranteed" to lower the energy; such a step

is not particularly appropriate in the case of a transition state. Consequently, transition state searches are usually much more sensitive to the local surface structure (number of negative hessian eigenvalues) than are minimum searches, and it is generally harder to find a transition state than a minimum.

The problem of finding transition states has been well served in the literature recently, with significant contributions from Cerjan and Miller,[8] Bell and Crighton[9] and, in particular, Simons and co-workers.[10,11] A good review of the various methods that have been used to locate transition states, from grid searches through quasi-Newton methods to conjugate gradient techniques, is given in ref. 9.

The purpose of this article is to present details of an efficient quasi-Newton like algorithm for locating transition states, based on the work of Simons et al.,[11] which has been made completely compatible with and "built in" to GAUSSIAN 82. Section I comprises a discussion of the formalism and the ideas behind it (full details are given in ref. 11); section II gives some details of the algorithm and its implementation within the framework of GAUSSIAN 82, and section III presents the results of applying the algorithm to find transition states for a number of chemical systems at the *ab initio* level.

I. DISCUSSION OF THE FORMALISM

The Taylor series expansion of the energy, E, at a point $X = X_0 + h$ about X_0 is

$$E = E_0 + g^\dagger h + \frac{1}{2} h^\dagger \mathbb{H} h + \ldots \quad (1)$$

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where E_0, $\mathbf{g}$, and $\mathbb{H}$ are the energy, gradient (vector), and hessian (matrix), respectively, at the point $\mathbf{X}_0$. Truncating this expansion at the quadratic term and applying the stationary condition $d\mathrm{E}/d\mathbf{h} = 0$ leads to the prediction that the best step $\mathbf{h}$ to take to get from the current point $\mathbf{X}_0$ to a stationary point is the Newton-Raphson (NR) step

$$\mathbf{h} = -\mathbb{H}^{-1}\mathbf{g} \qquad (2)$$

In terms of the eigenvectors $\mathbf{V}_i$ and eigenvalues b_i of the hessian, the NR step can be written as

$$\mathbf{h} = \sum - \overline{F}_i \mathbf{V}_i / b_i \qquad (3)$$

where $\overline{F}_i = \mathbf{V}_i^{\mathsf{t}}\mathbf{g}$ is the component of $\mathbf{g}$ along the local eigenmode $\mathbf{V}_i$.

In their analysis of the Newton-Raphson step, and as can be seen from eq. (3), Simons et al.[10] showed that the NR step is directed *opposite* to the gradient along each mode with a positive hessian eigenvalue and *along* the gradient for each mode with a negative eigenvalue. That is, it attempts to minimize along modes with positive hessian eigenvalues and maximize along modes with negative eigenvalues. For a transition state search, if you are in the region of the energy surface where the hessian has the required one negative eigenvalue, then the NR step is a good step to take since it is doing exactly what is desired, maximizing along one mode while minimizing along all the others. On the other hand, if the hessian does not have the desired local structure, then the NR step is not appropriate and you must somehow get out of the current region and back into a region where the hessian *does* have the correct structure. It is this dependence on the correct local hessian structure which is the great weakness of the standard transition state search algorithm incorporated in GAUSSIAN 82.

One of the earliest attempts to develop a transition state search algorithm that could take corrective action when in the wrong region of the energy surface was due to Poppinger,[12] who suggested that, if the hessian had all positive eigenvalues, the lowest hessian eigenvector be followed *uphill*, whereas if the hessian had two or more negative eigenvalues the eigenvector corresponding to the least negative eigenvalue be followed *downhill*. While this should certainly lead you back into the right region of

the energy surface, it suffers from the drawback that although you are maximizing/minimizing along *one* mode, essentially nothing much is happening along the other modes, unlike the NR step which (when appropriate) maximizes/minimizes along *all* modes simultaneously. Another drawback is that successive such "eigenvector following" steps tend to become linearly dependent, which degrades many of the commonly used procedures for updating the hessian. Consequently, there may be a better step than the one proposed by Poppinger.

Cerjan and Miller[8] have demonstrated that there is indeed such a step. A simple modification to the Newton-Raphson step is capable of guiding the current point away from its neighborhood in search of another stationary point with the required characteristics. This is

$$\mathbf{h} = \sum - \overline{F}_i \mathbf{V}_i / (b_i - \lambda) \qquad (4)$$

in which λ can be regarded as a shift parameter on the hessian eigenvalues b_i. Both Cerjan and Miller[8] and Simons et al.[10] have presented algorithms for locating transition states based on the above step, the only difference between them being the method adopted to determine the shift parameter λ. A more recent publication by Simons et al.[11] gives another prescription for choosing λ which has been found numerically to be the best of the three, and it is this method that has been used in the algorithm to be described here.

Basically Simons et al.[11] utilize a rational function approximation to the energy E, rewriting (1) as

$$\mathrm{E} - \mathrm{E}_0 = \frac{\mathbf{g}^{\mathsf{t}}\mathbf{h} + \dfrac{1}{2}\mathbf{h}^{\mathsf{t}}\mathbb{H}\mathbf{h}}{1 + \mathbf{h}^{\mathsf{t}}\mathbb{S}\mathbf{h}}$$

$$= \frac{\dfrac{1}{2}(\mathbf{h}^{\mathsf{t}}1)\begin{pmatrix}\mathbb{H} & \mathbf{g} \\ \mathbf{g}^{\mathsf{t}} & 0\end{pmatrix}\begin{pmatrix}\mathbf{h} \\ 1\end{pmatrix}}{(\mathbf{h}^{\mathsf{t}}1)\begin{pmatrix}\mathbb{S} & 0 \\ 0 & 1\end{pmatrix}\begin{pmatrix}\mathbf{h} \\ 1\end{pmatrix}} \qquad (5)$$

The symmetric matrix $\mathbb{S}$ (which takes a simple diagonal form) can be regarded as a scaling matrix.

Applying the stationary condition $d\mathrm{E}/d\mathbf{h} = 0$ to (5) yields the eigenvalue equation

$$\begin{pmatrix}\mathbb{H} & \mathbf{g} \\ \mathbf{g}^{\mathsf{t}} & 0\end{pmatrix}\begin{pmatrix}\mathbf{h} \\ 1\end{pmatrix} = \lambda\begin{pmatrix}\mathbb{S} & 0 \\ 0 & 1\end{pmatrix}\begin{pmatrix}\mathbf{h} \\ 1\end{pmatrix} \qquad (6)$$

Note that the dimensionality of (6) is $(n + 1)$ where n is the number of variables to be optimized. Expanding out (6) gives

$$(\mathbb{H} - \lambda\mathbb{S})\mathbf{h} + \mathbf{g} = \mathbf{0} \qquad (7a)$$

$$\mathbf{g}^{\mathsf{t}}\mathbf{h} = \lambda \qquad (7b)$$

In terms of a diagonal hessian representation, and with $\mathbb{S}$ a unit matrix, (7a) rearranges to (4), and substitution of (4) into the diagonal form of (7b) gives

$$\sum \bar{F}_i^2/(\lambda - b_i) = \lambda \qquad (8)$$

which can be used to evaluate λ.

Without going into too many details, the eigenvalues, λ, of the RFO matrix eq. (6) have the following properties[11]:

(i) The $(n + 1)$ eigenvalues of (6) bracket the (n) eigenvalues of the hessian $\lambda_i \leq b_i \leq \lambda_{i+1}$

(ii) At convergence to a *minimum* point all $\bar{F}_i = 0$ and hence $\mathbf{h} = \mathbf{0}$. The corresponding lowest eigenvalue λ_1 of the RFO matrix is also zero and the other n eigenvalues are those of the hessian at the minimum point. Thus, near a local minimum, λ_1 is negative and approaches zero at convergence.

(iii) For a saddle point of order μ the zero eigenvalue separates the μ negative and $(n - \mu)$ positive hessian eigenvalues. In particular for a transition state, the one negative hessian eigenvalue is separated from the $(n - 1)$ positive eigenvalues.

The separability of the positive and negative hessian eigenvalues led Simons et al. to suggest that the problem could be separated into μ principal modes to be maximized and $(n - \mu)$ modes to be minimized. Hence we could have two shift parameters, λ_P and λ_n, one for modes relative to which E is to be maximized and the other for which it is minimized. We could thus partition the RFO matrix into two smaller P-RFO matrices and solve each problem separately.

For a transition state, in terms of the hessian eigenmodes, this gives the two matrix equations

$$\begin{pmatrix} b_1 & \bar{F}_1 \\ \bar{F}_1 & 0 \end{pmatrix}\begin{pmatrix} h_1 \\ 1 \end{pmatrix} = \lambda_P\begin{pmatrix} h_1 \\ 1 \end{pmatrix} \qquad (9a)$$

$$\begin{pmatrix} b_2 & & \mathbb{0} & \bar{F}_2 \\ & \cdot & & \vdots \\ & & \cdot & \vdots \\ \mathbb{0} & & b_n & \bar{F}_n \\ \bar{F}_2 & \cdots & \bar{F}_n & 0 \end{pmatrix}\begin{pmatrix} h_2 \\ \vdots \\ \vdots \\ h_n \\ 1 \end{pmatrix} = \lambda_n\begin{pmatrix} h_2 \\ \vdots \\ \vdots \\ h_n \\ 1 \end{pmatrix} \qquad (9b)$$

λ_P is the *highest* eigenvalue of (9a); it is always positive and approaches zero at convergence. λ_n is the *lowest* eigenvalue of (9b); it is always negative and again approaches zero at convergence.

At a given point $\mathbf{X}_0$ then, the components of the step $\mathbf{h}$ to be taken to get to the next point (which, hopefully, will be a better estimate of the transition state than the current point) can be obtained from the eigenvector of (9a) corresponding to the highest eigenvalue λ_p (which gives h_1) and the eigenvector of (9b) corresponding to the lowest eigenvalue λ_n (which gives $h_2 \ldots h_n$). In practice $\mathbf{h}$ is *not* found in this way; instead the eigenvalues λ_P and λ_n are found [λ_P as the highest solution to a simple quadratic equation; λ_n iteratively via (8)] and $\mathbf{h}$ is then calculated from (4).

Having taken the step $\mathbf{h}$ into a new region of the energy surface, the local surface characteristics at the new point have to be determined. This involves updating (or recalculating) the hessian in order for it to be appropriate to the neighborhood of the new point as opposed to the old one. Since taking too large a step away from the old point invalidates any updating scheme (in addition to the fact that the bigger the step, the more the likelihood of moving out of the region for which the original hessian was itself valid), it is wise to set a maximum tolerance on the size of any calculated step $\mathbf{h}$, and scale $\mathbf{h}$ down accordingly if this maximum is exceeded. In ref. 11 Simons et al. recommend a dynamic step reduction procedure to deal with the problem of overstepping. This is based on a procedure suggested by Fletcher[13] in which the predicted energy change arising from taking the step $\mathbf{h}$ is compared with the actual energy change, and the step length reduced if the difference exceeds a certain tolerance. Simons et al. found that, due to the approximate nature of the hessian, such a step restrictive procedure should be used along with an updated hessian to mainly avoid an occasional large misleading step. However, in a previous work,[10] the opposite claim is made (admittedly with a different step length updating scheme) that an updated hessian is

simply not accurate enough to use in predicting the energy change resulting from a step **h**. In the algorithm described in the following section, it was found that the step reduction procedure given in ref. 11 often hindered convergence, reducing the step size unnecessarily; consequently only a maximum allowed stepsize was imposed. This involved setting the scaling matrix of (6) to a unit matrix, and doing any required scaling *after* calculating the step **h**. A maximum stepsize of 0.3 was found to work well in practice.

Mode Following

In calculating the best step **h** to take during a transition state search, it was assumed in (9a) and (9b) that maximization was to take place along the *lowest* hessian mode, b_1, and minimization along all the higher modes. However, as first pointed out by Cerjan and Miller,[8] it is possible to maximize along modes other than the lowest and in this manner obtain transition states for alternative rearrangements and/or dissociations from the *same* initial starting point. For maximization along the kth mode (instead of the lowest) (9a) would be replaced by

$$\begin{pmatrix} b_k & \overline{F}_k \\ \overline{F}_k & 0 \end{pmatrix} \begin{pmatrix} h_k \\ 1 \end{pmatrix} = \lambda_P \begin{pmatrix} h_k \\ 1 \end{pmatrix} \qquad (9c)$$

and (9b) would now exclude the kth mode but include the lowest.

Since what was originally the kth mode is the mode along which the negative eigenvalue is required, then this mode will eventually wind up as being the lowest mode at some stage of the optimization. To ensure that the original mode is being followed smoothly from one iteration to the next, the mode that is actually followed is the one that has the greatest overlap with the mode followed on the previous cycle. When this mode has become the lowest mode, thereafter it is always the lowest mode that is followed.

Mode following as described above has been incorporated into the algorithm; however, although it can prove useful, it is by no means obvious what mode to follow at any given point in order to locate a transition state of a desired type. This will be discussed in more detail in Section III. It should be noted that there are virtually always more variables (and hence more modes) in a given system

than there are transition structures associated with that system; hence following *every* mode is bound to lead to duplication (i.e., finding a transition state that has already been located by following a previous mode) if, indeed, it leads to anything at all.

II. THE ALGORITHM

The algorithm is comprised of the following steps:

(1) Make an initial guess **X** at the position of the transition state. Calculate (or estimate) the gradient vector **g** and the hessian matrix H at the initial point. Within GAUSSIAN 82 analytical gradients are available for SCF, MP2, CID and CISD wave functions. For SCF wave functions, analytical second derivatives are also available, and hence an exact hessian can be calculated at the first point. For the other wave functions, the hessian can be estimated by stepping through each variable and doing a finite-difference calculation on the gradient. It is often advantageous to use the hessian from a previous calculation at a lower level of theory, or with a smaller basis set, as the starting hessian for a higher level calculation.

(2) Diagonalize the Hessian ($\mathsf{H}' = \mathsf{U}^t\mathsf{H}\mathsf{U}$) and determine the local surface characteristics (number of negative eigenvalues). Transform **g** into the local hessian modes $\overline{\mathbf{F}} = \mathsf{U}^t\mathbf{g}$.

(3) Depending on the structure of the hessian determine what type of step to take. If the hessian has the wrong number of negative eigenvalues, this will be the P-RFO step [see (9)]. If mode following has been switched on, then, on the first step, save the eigenvector corresponding to the mode being followed. On subsequent steps determine which hessian mode has the greatest overlap with the eigenvector followed on the previous cycle, and save and follow this mode. If mode following has *not* been switched on, follow the lowest mode. Form λ_p from (9c) (k is the mode being followed)

$$\lambda_p = \frac{1}{2} b_k + \frac{1}{2} \sqrt{(b_k^2 + 4\overline{F}_k^2)}$$

and then form **h** from (4) as

$$\mathbf{h}_k = -\overline{\mathbf{F}}_k \mathbf{V}_k/(b_k - \lambda_p)$$

$$\mathbf{h}_i = -\overline{\mathbf{F}}_i \mathbf{V}_i/(b_i - \lambda_n) \qquad i = 1\ldots n$$
$$i \neq k$$

$$\mathbf{h} = \sum_{j=1}^{n} \mathbf{h}_j$$

Note that, not only must λ_n be negative, but, due to the bracketing property, it must be lower than b_2 (if the lowest mode is being followed) or lower than b_1 (if some other mode is being followed). Care must be taken that this is so, especially if the hessian has two or more negative eigenvalues (in which case b_2 will be negative).

If the hessian has the correct structure (one negative eigenvalue) then, as mentioned in Section I, it is possible to take the Newton-Raphson step, although the P-RFO step is still the recommended one. The option is available (see Table I) of taking either of the two steps in this case.

Table I. Options available for OPT = EF.

```
C   OPTIONS            COMMON/IOP/
C
C
C   IOP(5)      nature of required stationary point
C               0     find a TS                              (default)
C               1     find a minimum
C
C   IOP(6)      maximum number of steps allowed
C               0     min(40,nvar+20)                        (default)
C                     (where nvar = number of variables)
C               N     N steps
C
C   IOP(7)      convergence criteria on RMS gradient
C               0     0.0003                                 (default)
C               N     0.001/N
C               note: the other convergence criteria are
C               maximum gradient = 1.5 * RMS gradient
C               RMS displacement = 4.0 * RMS gradient
C               max displacement = 1.5 * RMS displacement
C
C   IOP(8)      maximum stepsize allowed during optimization
C               0     DMAX = 0.3                             (default)
C               N     DMAX = 0.01*N
C
C   IOP(10)     input of initial second derivative matrix
C               all values must be in atomic units
C               0     estimate entire Hessian numerically  (TS default)
C                     estimate diagonal elements only      (MIN default)
C               1     read in full FRCNST matrix (lower triangle)
C                     format (8F10.6)
C               2     read in selected elements of FRCNST
C                     READ I,J,FRCNST(I,J)           2I3, F20.0
C               3     read FRCNST matrix from the checkpoint file
C               4     calculate Hessian analytically
C               5     read cartesian force constants from checkpoint file
C
C   IOP(11)     Hessian recalculation
C               0     update the Hessian only               (default)
C               N     recalculate the Hessian (analytically if
C                     possible, else numerically) every N points
C               (OBS! if this option is invoked, restarts from the
C               checkpoint file should NOT be attempted except via a
C               nonstandard route. EXCEPTION: analytical derivatives
C               at all points via CALCALL can be restarted)
C
C   IOP(13)     type of Hessian update
C               0     Powell update                        (TS default)
C               1     BFGS update                          (MIN default)
C               2     BFGS update with safeguards to ensure retention
C                     of positive definiteness
C
C   IOP(16)     maximum allowable magnitude of the Hessian eigenvalues
C               if this magnitude is exceeded, the eigenvalue is replaced
C               0     EIGMAX = 25.0                          (default)
C               N     EIGMAX = 0.1*N
```

Table I (continued)

```
C
C   IOP(17)     minimum allowable magnitude of the Hessian eigenvalues
C               similar to IOP(16)
C               0    EIGMIN = 0.0001                         (default)
C               N    EIGMIN = 1.0/N
C
C   IOP(19)     search selection
C               0    P-RFO or RFO step only                 (default)
C               1    P-RFO or RFO step for "wrong" Hessian
C                    otherwise Newton-Raphson
C
C   IOP(21)     expert switch
C               0    normal          mode                   (default)
C               1    expert          mode
C                    certain cutoffs to control optimization relaxed
C
C   IOP(33)     print option
C               0    on                                     (default)
C               1    off turns off extra printing
C               (default of "on" by popular request)
C
C   IOP(34)     dump option
C               0    off                                    (default)
C               1    on turns on debug printing
C
C   IOP(35)     restart option
C               0    normal optimization                    (default)
C               1    first point of a restart
C                    recover geometry etc. from checkpoint file
C
C   IOP(36)     checkpoint option
C               0    checkpointing as normal                (default)
C               1    suppress checkpointing
C
C   IOP(37)     d2e cleanup option
C               0    no special action taken                (default)
C               1    this is the last point at which analytical
C                    derivatives are available; clean up the RWF file
C
C
C   MODE FOLLOWING: mode following is turned on via the IC array, which
C   is input with the Z-matrix variables in Link 101. Adding 4 to the IC
C   entry for a particular variable will cause a transition state search
C   to follow the Hessian mode with the largest magnitude component for
C   that variable. Adding 10 to the IC entry for the Kth variable will
C   follow the Kth Hessian mode. ONLY ONE IC ENTRY SHOULD BE MODIFIED IN
C   THIS WAY, I.E., ONLY ONE MODE SHOULD BE FOLLOWED AT A TIME.
```

Although the discussion given here concerns the location of transition states, the algorithm can be used equally well to locate minima, in which case the simple RFO step, involving minimization along *all* modes and only one shift parameter λ, is the step to take.

(4) Having determined the step **h**, check that $|\mathbf{h}| \leq$ DMAX, where DMAX is a user supplied tolerance on the step-size. As mentioned previously, the default is DMAX = 0.3. If $|\mathbf{h}| >$ DMAX, then scale the step down so that $|\mathbf{h}|$ = DMAX.

(5) Check for convergence. GAUSSIAN 82 has four criteria that must be satisfied before convergence is attained; the largest magnitude components of the gradient vector **g** and the displacement vector **h**, and the root mean square gradient and displacements must all be below user supplied tolerances. If all four of these criteria are satisfied, then stop with the current point **X** as the position of the transition state.

(6) If the convergence criteria are not satisfied, then provided the total number of steps taken has not exceeded a predefined limit MAXSTEP, take the step given by **h**, i.e., set $\mathbf{X}' = \mathbf{X} + \mathbf{h}$. Calculate the energy E and gradient vector **g**' at the new point. If convergence has not been attained after MAXSTEP steps, stop. (GAUSSIAN 82 has a "checkpointing" option which ensures

that all the information needed for a restart is saved; thus the transition state search can be restarted from where it left off if desired by simply increasing MAXSTEP).

(7) Update (or recalculate) the hessian matrix H. Note that the option is available (option 11, Table I) of recalculating the hessian every N steps; otherwise it will simply be updated. The update depends on the gradient vector at the old point, g, the gradient vector at the new point g', and the displacement vector (the step) h. There are many formulae in the numerical analysis literature for hessian updates (e.g., see ref. 13) and two alternative updates have been included in the algorithm; these are the so-called Powell update[14] which is given by

$$H^{new} = H^{old} + \frac{1}{(h^\dagger h)}$$

$$\cdot \left[Vh^\dagger + hV^\dagger - \frac{(V^\dagger h)(hh^\dagger)}{(h^\dagger h)} \right]$$

where

$$V = (g' - g - H^{old}h)$$

and the BFGS update[13] which is

$$H^{new} = H^{old} + \frac{VV^\dagger}{(V^\dagger h)} - \frac{(H^{old}h)(h^\dagger H^{old})}{h^\dagger H^{old}h}$$

with $V = (g' - g)$

The BFGS update is generally regarded as the best update to use for a minimum search, and consequently (see option 13, Table I) is the default in this case. For a transition state search, the Powell update is the default.

It is often stated in the *Chemical* literature that the BFGS update will preserve positive definiteness, i.e., if the hessian before the update is positive definite (all the eigenvalues are positive), then the updated hessian will also have this property (within the limitations of numerical round off error). Although this is true in general, it is *not* rigorously guaranteed for every possible step h and, in particular, is unlikely to hold if the quantity $(V^\dagger h)$ in the above updating formula is negative. However, the BFGS update is much more likely to favor retention

of a positive definite hessian than the Powell update, and for this reason is not recommended for a transition state search. The Powell update has no particular bias towards positive definiteness and is more flexible with regard to alteration of the hessian eigenvalue structure.

(8) Return to step (2) with the new hessian.

As implemented on VAX or IBM hardware, the GAUSSIAN 82 program package consists of a number of individual programs or "links", each of which is responsible for a certain part of the total *ab initio* calculation; for example evaluating integrals, performing an SCF calculation, transforming integrals or whatever. These links are "chained" in and out of machine memory at run time. In order to completely determine the course of a particular calculation, the sequence of links and the order in which they are to be executed must be specified. This can be done by either reading in the links in the desired order or by giving a few simple key words on a single command line which causes the required route to be generated internally by the program. Thus specifying "OPT" along with an *ab initio* procedure, say "RHF", and a basis set "3-21G" will generate the route for an optimization at the restricted (closed shell) Hartree-Fock level using the 3-21G split-valence gaussian basis set. "OPT=TS" will generate the route for a transition state search using the default algorithm supplied with GAUSSIAN 82. In line with this, the algorithm described here has been given a key word, and is invoked by the command "OPT=EF".

With each link, it is possible to supply a list of options which govern the behavior of the program within that link. The options currently available for "OPT=EF" are shown in Table I. This algorithm has been incorporated into the GAUSSIAN 82 package used in our group, and the options given and the structure of the algorithm in general adhere to the framework and philosophy of GAUSSIAN 82 as a whole.

III. APPLICATIONS

OPT=EF has now been used to locate a large number of transition states for a wide variety of reactions studied at the SCF level.

Several examples are presented below. Some of these have been selected to illustrate various advantages of the algorithm and to contrast it with the standard OPT = TS algorithm; others are taken from recent work within the group. In all cases the initial hessian was calculated analytically. For each example initial starting and final transition state geometries are given, together with the number of cycles to reach convergence (if attained). For the first four examples comparisons are given with two alternative algorithms; these are TS (the standard GAUSSIAN 82 algorithm) and POP [Poppinger's algorithm (12)]. The convergence criteria were the standard default values of 0.0003 on the RMS gradient; 0.00045 on the maximum gradient; 0.0012 on the RMS displacement and 0.0018 on the maximum displacement. For EF the default options given in Table I were used except for the initial hessian (IOP(10) = 4). All calculations were carried out on a VAX 11/750.

A. HCN ↔ HNC RHF/3-21G

This rearrangement has become something of a standard and is often used to test various transition state search procedures. It was studied by Bell and Crighton[9] with their hybrid conjugate gradient/quasi-Newton algorithm and also by Muller and Brown[15] using their constrained simplex optimization to give two recent examples. As indicated above,

the calculations done here are at the RHF level using the 3-21G basis set.

The initial geometry here was the "midpoint" between the HCN and HNC minima. At this geometry the hessian had one negative eigenvalue. All three algorithms perform well and converge in essentially the same manner onto the transition state with no apparent problems.

B. HCCH ↔ CCH₂ RHF/3-21G

Another standard example. The acetylene/ethenylidine rearrangement has been studied by Poppinger in the original presentation of his algorithm,[12] by Muller and Brown[15] and also Cejan and Miller.[8]

Both TS and EF perform very well for this system. POP, however, performs badly in comparison, taking twice as many cycles to converge as the other two algorithms. The poor performance of Poppinger's algorithm for this system was noted in ref. 8.

The above two systems were not expected to cause problems for the standard GAUSSIAN 82 algorithm, since the initial guess in each case was within the quadratic region of the transition structure, i.e., the hessian had one negative eigenvalue. We turn now to some examples where this is not the case.

C. $FH_3^+ ↔ FH_2^+ + H$ UHF/6-31G*

This is a somewhat unusual reaction, and in fact the structure obtained is not a true

Table II. Starting geometry, final geometry, and convergence for the HCN ↔ HNC transition state.

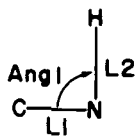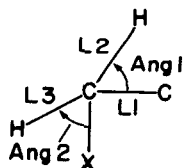|	Starting		Final
L1	1.14838		1.183
L2	1.58536		1.408
Ang1	90.0		55.1
cycles to converge:	TS 10	POP 9	EF 8

Table III. Starting geometry, final geometry, and convergence for the HCCH ↔ CCH₂ transition state. (X is a dummy to help with geometry specification)

	Starting		Final
L1	1.24054		1.247
L2	1.65694		1.428
L3	1.06318		1.056
Ang1	60.3568		54.2
Ang2	60.3568		86.6
cycles to converge:	TS 8	POP 15	EF 7

transition state; vibrational analysis reveals two imaginary frequencies. However, within the imposed symmetry constraints (C_2V) the hessian has only one negative eigenvalue.

Here the initial hessian had two negative eigenvalues. If the hessian eigenvalue structure is inappropriate for the type of stationary point sought, the default for TS is to halt the optimization; this can be overridden and the algorithm forced to continue. In this event any eigenvalues with the wrong signature simply have their signs reversed, and the new step is calculated in the normal manner. For this particular system this simple expedient worked well, and the performance of TS is only marginally worse than that of EF. However, this procedure is *not* recommended and can go badly wrong, as illustrated by the next example.

D. FCN ↔ FNC RHF/STO-3G

This is the fluorine analog of the HCN ↔ HNC rearrangement. It was studied by Bell and Crighton[9] who found that, on a semi-empirical INDO surface, the quasi-Newton algorithms they tried failed completely to find the transition state. This is not at all the case on *ab initio* surfaces, and preliminary work showed that, at least with a reasonable starting guess, all three algorithms compared here were easily able to locate the transition state. However, for a more stringent test, the transition state search was started with a geometry very near that of one of the minima, FCN, as shown in Table V.
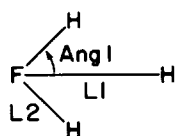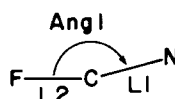
The initial hessian, not surprisingly, had all positive eigenvalues. Both EF and POP managed to move away from the region of the FCN minimum and into a region where the hessian had one negative eigenvalue in about half a dozen steps; thereafter both algorithms converged smoothly to the transition state. TS on the other hand consistently took poor or misguided steps and finally halted after 11 cycles as the gradient vector became too large: at this point the RMS gradient was 0.752 and the geometrical parameters were L1 = 1.222, L2 = 1.327 and Ang1 = 55.4.

E. Mode Following The CH_2FH^+ ylid ion

Ylid ions have been the subject of considerable theoretical and experimental attention recently, in many cases being more stable in the gas phase than their classical counterparts.[16] In their study of the methylene-fluoronium ion, Bouma et al.[17] reported two transition states at the UHF/3-21G level: a hydrogen bridged structure for the conversion of CH_2FH^+ to CH_3F^+ and another structure for the loss of hydrogen $CH_2FH^+ \rightarrow CH_2F^+ +$ H. They also found that the methylene cation (CH_2^+) and hydrogen fluoride collapse without activation to CH_2FH^+. Here an attempt is made to duplicate these results by starting from essentially the CH_2FH^+ minimum and following each of the hessian modes in turn in the manner described in the previous section.

The minimum and transition state geometries are shown in Table VI. With Cs symmetry maintained throughout, there are six

Table IV. Starting geometry, final geometry, and convergence for the $FH_3^+ \leftrightarrow FH_2^+ +$ H transition state.

	Starting	Final
L1	2.5	1.950
L2	1.6	1.246
Ang1	50.0	27.8
cycles to converge:	TS 13	POP 16 EF 11

Table V. Starting geometry, final geometry and convergence for the FCN ↔ FNC transition state.

	Starting	Final
L1	1.2	1.291
L2	1.3	1.449
Ang1	170.0	81.8
cycles to converge:	TS failed	POP 15 EF 13

Table VI. Geometry for the minimum, bridged transition structure and dissociative transition structure on the CH_2FH^+ surface.
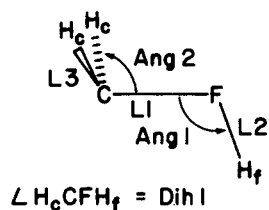
	Minimum	Bridged TS	Dissociative TS
L1	1.594	1.495	1.319
L2	0.967	1.252	1.514
L3	1.069	1.072	1.070
Ang1	125.1	58.0	131.7
Ang2	104.3	111.1	115.7
Dih1	109.1	104.6	86.2

variables and hence six possible hessian modes to follow.

Following mode 1 initially led to a decrease in Ang1; however, this quickly changed to an increase in L1, the C-F bond length, and dissociation to CH_2^+ + HF occurred without locating a transition structure along the Cs pathway. After 20 cycles the C-F bond length was over 4A and the CFH angle (Ang1) almost 180. This strongly suggests that there is unlikely to be a transition state for this dissociation, in agreement with the results of ref. 17.

After two steps following mode 2, this mode became the lowest and convergence to the bridged transition state was achieved after 24 cycles. At the 3-21G level, this transition state is 215 kJmol^{-1} above the CH_2FH^+ minimum.

The dissociative transition state was located by following mode 4. As with mode 2, this mode became the lowest after two steps and convergence was attained after just 13 cycles. This transition state lies 253 kJmol^{-1} above the minimum.

Following modes 3 and 5 led to the "crashing" of two or more atoms: for mode 3 the two hydrogen atoms H_c due to the continual increase in the dihedral angle Dih1; for mode 5 these atoms and fluorine as a result of the steady decrease in Ang2, whilst following mode 6 gave rise to a continuous increase in L3 and complete breakup of the CH_2FH^+ moiety into a CFH^+ fragment and two separate hydrogen atoms.

Note that — apart from the reversal of modes 3 and 4 — following the *lowest* modes led to the transition states/dissociation products, and these were obtained in order of their relative energies, i.e., mode 1 gave CH_2^+ + HF (204 kJmol^{-1} above the methyfluoronium ion), mode 2 gave the bridged

transition state (215 kJmol^{-1}) and mode 4 the dissociative transition state (253 kJmol^{-1}).

Although mode following seems to be fairly successful — leading to both the transition states characterized by Bouma et al.[17] and also indicating that there is no transition state for dissociation into the methylene cation and hydrogen fluoride — it is clear that a more sensible guess for the transition state being sought would significantly reduce the number of cycles required for convergence. However, in cases where it is not so obvious what the transition state should be, or whether there is a transition state at all, then mode following could prove particularly valuable in helping to characterize the energy surface.

F. Minimization CH3F RHF/3-21G

Finally, to indicate that the algorithm is also able to locate minima efficiently, an optimization on methyl fluoride is presented starting from a very poor initial geometry

Convergence was attained in 11 cycles, the same as with the standard GAUSSIAN 82 minimization algorithm (GRAD). Unlike the case for the transition state searches (A-E) the initial hessian was not calculated analytically; OPT=GRAD has a built-in algorithm for estimating the hessian depending on the various atoms present in the molecule, and their initial bond lengths and angles, and this algorithm — again due to Schlegel[18] — has been incorporated into OPT=EF. Thus both the optimizations started with the same (diagonal) hessian. This example, and many other calculations done in the group, indicate that OPT=EF is competitive with OPT=GRAD for the location of minima.

Table VII. Starting geometry, final geometry, and convergence for methyl fluoride.
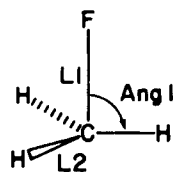
	Starting	Final
L1	2.0	1.404
L2	1.6	1.079
Ang1	90.0	109.4
cycles to converge:	EF 11	GRAD 11

SUMMARY

An efficient quasi-Newton algorithm for locating transition states, based on the work of Simons et al.,[11] has been presented. The algorithm has been designed for, and is completely compatible with, the GAUSSIAN 82 *ab initio* program package developed by Pople et al.[6] It is capable of locating transition states even if started in the wrong region of the energy surface and, by invoking hessian mode following, can locate transition states for alternative rearrangement/dissociation reactions from the same initial starting point (e.g., the minimum). It can also be used to locate minima.

AVAILABILITY OF CODE

The FORTRAN code for the above algorithm is available and can be supplied, along with the modifications needed to run in a GAUSSIAN 82 environment, on request. Both VAX and IBM versions exist. Eventually it is intended to submit the algorithm to QCPE for distribution or something along similar lines; in the meantime all interested users should contact the author directly.

The earlier work of Cerjan and Miller[8] from which many of the later developments have stemmed, and that of Simons and co-workers[10,11] on which this algorithm is based, must clearly be acknowledged.

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