

# On finding transition states

Charles J. Cerjan<sup>a)</sup> and William H. Miller

Department of Chemistry and Materials and Molecular Research Division of the Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

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An algorithm for locating transition states on a potential energy surface is described. The most important feature of the algorithm, which makes explicit use of the second derivative matrix of the potential surface, is that it is able to "walk uphill" from the minimum on a potential surface to the transition state essentially automatically. The method is illustrated by application to a two dimensional model problem, to the vinylidene-acetylene rearrangement ( $\text{H}_2\text{C}=\text{C} \leftrightarrow \text{HC}\equiv\text{CH}$ ), and to the dissociation and rearrangement of formaldehyde ( $\text{H}_2\text{CO} \leftrightarrow \text{H}_2 + \text{CO}$ ,  $\text{HCOH}$ ). The algorithm is also seen to provide an improved way of following a reaction path from a transition state down to reactants or products.

## I. INTRODUCTION

Continuing developments in the computational methodology of quantum chemistry make the *a priori* description of chemical reaction dynamics an increasingly practical possibility. The object of such calculations is the Born-Oppenheimer potential energy surface (or surfaces) which govern the dynamical process of interest.

For reactions involving more than three or four atoms, however, knowledge of the complete potential surface as a function of all  $3N-6$  nuclear coordinates ( $N$ =number of atoms) is usually out of the question, and effort is most often focused on determining special features of the potential surface, e.g., absolute and local minima on the surface, and the saddle points (i.e., transition states) that separate them. Because methods are now available for the efficient calculation of the *gradient*<sup>1</sup> of the potential with respect to nuclear coordinates, it is also becoming feasible to follow the reaction path<sup>2</sup> (the steepest descent path in mass-weighted Cartesian coordinates) from a saddle point down to the minima on the surface. On the basis of the reaction path, and the matrix of force constants along it, one can construct a dynamical model which describes many attributes of the polyatomic reaction dynamics.<sup>3</sup>

The purpose of this paper is to suggest and illustrate a systematic algorithm for finding transition states on potential surfaces and also for generating the reaction path connecting a transition state and a local (or absolute) minimum on the surface. The basic element of the algorithm is to make a local quadratic approximation to the potential surface at each point along the reaction path, and its most important feature is that it is a stable algorithm for walking uphill from a minimum on the potential surface to a transition state.

Previous attempts to locate transition states have concentrated on gradient norm minimization<sup>4,5</sup> or energy minimization.<sup>6</sup> The norm minimization technique has several disadvantages which arise because it is basically a root search technique, so that convergence to a transition state is not assured—only convergence to a zero of the potential gradient. Associated with the convergence difficulty is the requirement that a good initial guess

must be supplied, otherwise a large number of steps may be required for convergence. Also, in cases where chemical intuition fails, there is no systematic prescription for searching for a transition state. Similarly, energy minimization will have stability difficulties if the surface is complicated, and may also require a large number of energy evaluations to be effective.

Section II first discusses the qualitative ideas of the algorithm and also develops it in general form. Since the approach requires at each step the force constant (i.e., second derivative) matrix of the potential as well as the gradient (i.e., first derivative), an efficient method for direct calculation of the force constant matrix, as well as the gradient, is necessary for it to be a truly practical approach. Pople *et al.*<sup>7</sup> have in fact reported the development of such methods within the SCF approximation, and there is intense work in several groups on extending such capabilities to more general, e.g., MCSCF and general CI, wave functions. The present paper is thus looking ahead to the availability of such techniques.

Applications of the algorithm of Sec. II to "walking uphill" from a minimum to a transition state are described in Sec. III; the problems chosen are a model problem which has some particularly pathological features, and two molecular systems  $\text{C}_2\text{H}_2$  and  $\text{H}_2\text{CO}$ . It is also shown, by application to the  $\text{HNC} \rightarrow \text{HCN}$  reaction, that the algorithm provides a much more efficient and accurate procedure for following the reaction path from a transition state down to a minimum than by simply following the gradient vector itself.

## II. THEORETICAL CONSIDERATIONS

### A. Qualitative discussion

To motivate the development below, consider a potential surface as sketched in Fig. 1; there are  $F=2$  degrees of freedom, and  $x_1$  and  $x_2$  are the two mass-weighted Cartesian coordinates of the system. The point  $\mathbf{a}=(a_1, a_2)$  at the center of the circle is near, but not on, the steepest descent path (i.e., the reaction path).

The goal is to step from position  $\mathbf{a}$  to a new position  $\mathbf{x}$  that is on (or at least very close to) the reaction path in the uphill direction; i.e., we wish to march uphill along the reaction path toward a transition state. (There may, of course, exist no transition state, but if there does

<sup>a)</sup>Present address: Department of Chemistry, University of Chicago, Chicago, Illinois 60637.

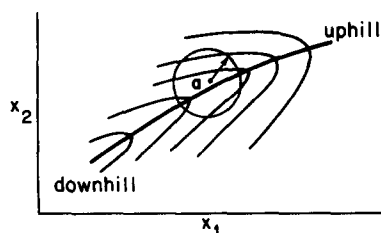


FIG. 1. Contour plot of a potential surface  $V(x_1, x_2)$ . The heavy curve is the reaction path, and the point  $\mathbf{a} = (a_1, a_2)$  is close to it. The circle of radius  $\Delta$  about  $\mathbf{a}$  indicates the locus of possible steps  $\mathbf{x}-\mathbf{a}$ .

then it will be reached in this manner.)

First consider the situation if one makes a linear approximation to the potential about the point  $\mathbf{a}$ :

$$V(\mathbf{x}) = V(\mathbf{a}) + D_1(\mathbf{a})\Delta x_1 + D_2(\mathbf{a})\Delta x_2, \quad (2.1)$$

where

$$D_i(\mathbf{a}) = \left( \frac{\partial V(\mathbf{x})}{\partial x_i} \right)_{\mathbf{x}=\mathbf{a}}, \quad \Delta x_i = x_i - a_i.$$

If we consider a step  $\Delta \mathbf{x}$  of fixed length  $\Delta$ , the radius of the circle about  $\mathbf{a}$  in Fig. 1, then the increment  $\Delta \mathbf{x}$  can be parametrized as

$$\Delta x_1 = \Delta \cos \theta, \quad (2.2a)$$

$$\Delta x_2 = \Delta \sin \theta, \quad (2.2b)$$

where  $\theta$  is the angle which specifies the direction of the increment  $\Delta \mathbf{x}$ . As a function of  $\theta$ , the linearized approximation to the potential is

$$V(\theta) - V(\mathbf{a}) = \Delta(D_1 \cos \theta + D_2 \sin \theta), \quad (2.3)$$

i.e., a simple harmonic as sketched in Fig. 2(a). The angle  $\theta_x$  for which  $V(\theta)$  is a maximum is

$$\tan \theta_x = D_2/D_1,$$

which leads to a step  $\Delta \mathbf{x}$  proportional to the gradient

$$\Delta \mathbf{x} \propto \frac{\partial V(\mathbf{a})}{\partial \mathbf{a}}. \quad (2.4)$$

As is clear from Fig. 1, if the point  $\mathbf{a}$  were exactly on the reaction path, then the gradient vector would indeed point in the correct direction, i.e., uphill along the reaction path, but if it is only slightly off the reaction path then the gradient direction diverges from the reaction path. This defocusing nature of trying to follow the gradient vector uphill is well known.

If, however, the second derivative matrix of  $V$  at point  $\mathbf{a}$  is available, then a second-order Taylor's series expansion is possible:

$$V(\mathbf{x}) = V(\mathbf{a}) + D_1(\mathbf{a})\Delta x_1 + D_2(\mathbf{a})\Delta x_2 + \frac{1}{2}K_{11}(\mathbf{a})\Delta x_1^2 + \frac{1}{2}K_{22}(\mathbf{a})\Delta x_2^2 + K_{12}(\mathbf{a})\Delta x_1 \Delta x_2, \quad (2.5)$$

where

$$K_{ij}(\mathbf{a}) = \left( \frac{\partial^2 V}{\partial x_i \partial x_j} \right)_{\mathbf{x}=\mathbf{a}}.$$

Again considering a step  $\Delta \mathbf{x}$  of fixed length, as param-

etrized by Eq. (2.2), the variation of the potential with the direction of the step, i.e., with  $\theta$ , has second as well as first harmonics as follows:

$$V(\theta) = V(\mathbf{a}) + \Delta(D_1 \cos \theta + D_2 \sin \theta) + (\Delta^2/2)(K_{11} \cos^2 \theta + K_{22} \sin^2 \theta + 2K_{12} \sin \theta \cos \theta); \quad (2.6a)$$

the last term in the above equation can also be written as

$$(\Delta^2/2) \left[ \frac{1}{2}(K_{11} + K_{22}) + \frac{1}{2}(K_{11} - K_{22}) \cos(2\theta) + K_{12} \sin(2\theta) \right]. \quad (2.6b)$$

Figure 2(b) shows the qualitative behavior of  $V(\theta)$ , the most important feature being that the quadratic terms in the expansion of  $V$  (i.e., the second harmonics in  $\theta$ ) lead to four extrema of  $V(\theta)$ , two local maxima and two local minima. It is clear that the direction of interest is the angle  $\theta_x$  indicated in Fig. 2(b) which corresponds to the local minimum of  $V(\theta)$  which is not the absolute minimum (which is the downhill direction). The angles  $\theta$  corresponding to the two local maxima in Fig. 2(b) are the directions up the sides of the harmonic valley about the reaction path.

For the above arguments to be applicable, the length of the step  $\Delta$  cannot be too small, or else the quadratic terms in Eq. (2.6) will be too small compared to the linear terms to produce a  $V(\theta)$  with four extrema. Too large a step size will be bad, however, for the quadratic approximation to  $V$  would be poor. It is intuitively clear, therefore, that an intermediate value of  $\Delta$  is required—not too large, not too small—for the algorithm to be meaningful. Furthermore, since the direction  $\theta_x$  in Fig. 2(b) is sandwiched between the two local maxima, which are the directions up the sides of the valley, it is also intuitively clear that choosing the increment  $\Delta \mathbf{x}$  in the direction  $\theta_x$  provides a stable algorithm for walking uphill to the transition state.

## B. General development

To implement these ideas more generally, we approximate  $V(\mathbf{x})$  about the point  $\mathbf{a}$  quadratically, as follows:

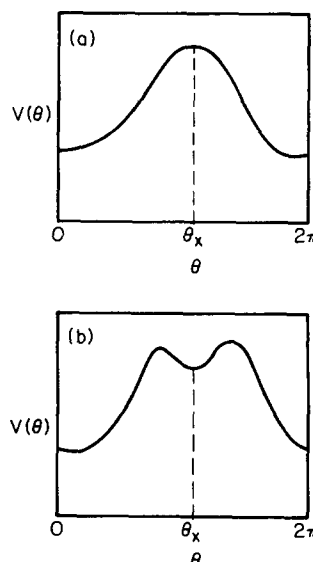


FIG. 2. (a) Variation of the potential as a function of  $\theta$  (i.e., along the circle about  $\mathbf{a}$  in Fig. 1) for the linear approximation to the potential [Eq. (2.3)]. (b) Same as 2(a), but for the quadratic approximation to the potential [Eq. (2.6)].

$$V(\mathbf{x}) \equiv V(\Delta\mathbf{x}) = V_0 + \mathbf{D} \cdot \Delta\mathbf{x} + \frac{1}{2} \Delta\mathbf{x} \cdot \mathbf{K} \cdot \Delta\mathbf{x}, \quad (2.7)$$

where, as before,

$$V_0 = V(\mathbf{a}), \quad (2.8a)$$

$$\mathbf{D} = \frac{\partial V(\mathbf{a})}{\partial \mathbf{a}}, \quad (2.8b)$$

$$\mathbf{K} = \frac{\partial^2 V(\mathbf{a})}{\partial \mathbf{a} \partial \mathbf{a}}, \quad (2.8c)$$

and then look for extrema of  $V(\Delta\mathbf{x})$  subject to the constraint of a fixed step size  $\Delta$ :

$$\Delta\mathbf{x} \cdot \Delta\mathbf{x} = \Delta^2. \quad (2.9)$$

This is most easily carried out in general with the use of a Lagrange multiplier.

Thus consider the Lagrange function  $L(\Delta\mathbf{x}, \lambda)$ :

$$L(\Delta\mathbf{x}, \lambda) = V_0 + \mathbf{D} \cdot \Delta\mathbf{x} + \frac{1}{2} \Delta\mathbf{x} \cdot \mathbf{K} \cdot \Delta\mathbf{x} + (\lambda/2)(\Delta^2 - \Delta\mathbf{x} \cdot \Delta\mathbf{x}), \quad (2.10)$$

$\lambda$  being the Lagrange multiplier. The equations determining the extrema are

$$\frac{\partial L}{\partial \Delta\mathbf{x}} = 0$$

$$\frac{\partial L}{\partial \lambda} = 0,$$

which gives

$$0 = \mathbf{D} + \mathbf{K} \cdot \Delta\mathbf{x} - \lambda \Delta\mathbf{x}, \quad (2.11a)$$

$$0 = \Delta^2 - \Delta\mathbf{x} \cdot \Delta\mathbf{x}. \quad (2.11b)$$

Equation (2.11a) gives

$$\Delta\mathbf{x} = (\lambda \mathbf{1} - \mathbf{K})^{-1} \cdot \mathbf{D}, \quad (2.12)$$

and then Eq. (2.11b) reads

$$\Delta^2 = \mathbf{D} \cdot (\lambda \mathbf{1} - \mathbf{K})^{-1} \cdot \mathbf{D}. \quad (2.13a)$$

Eq. (2.13a) is an algebraic equation for  $\lambda$ , and once  $\lambda$  is determined from it for a given value of  $\Delta$ , Eq. (2.12) gives the step size  $\Delta\mathbf{x}$ . The value of  $V(\Delta\mathbf{x})$  with  $\Delta\mathbf{x}$  given by Eq. (2.12) is

$$V(\Delta\mathbf{x}) \equiv V(\lambda) = V_0 + \mathbf{D} \cdot (\lambda \mathbf{1} - \mathbf{K})^{-1} \cdot \mathbf{D} + \frac{1}{2} \mathbf{D} \cdot (\lambda \mathbf{1} - \mathbf{K})^{-1} \cdot \mathbf{K} \cdot (\lambda \mathbf{1} - \mathbf{K})^{-1} \cdot \mathbf{D},$$

or

$$V(\lambda) - V_0 = \mathbf{D} \cdot (\lambda \mathbf{1} - \mathbf{K})^{-1} \cdot (\lambda \mathbf{1} - \frac{1}{2} \mathbf{K}) \cdot (\lambda \mathbf{1} - \mathbf{K})^{-1} \cdot \mathbf{D}. \quad (2.13b)$$

Equation (2.13) takes a simpler form if one introduces the unitary matrix  $\mathbf{U}$  that diagonalizes  $\mathbf{K}$ :

$$\mathbf{U}^\dagger \cdot \mathbf{K} \cdot \mathbf{U} = \mathbf{k}, \quad (2.14)$$

where  $\mathbf{k}$  is diagonal. If  $\mathbf{d}$  is defined by

$$\mathbf{d} = \mathbf{U}^\dagger \cdot \mathbf{D},$$

then Eq. (2.13) reads

$$\Delta^2 = \Delta^2(\lambda) \equiv \sum_{i=1}^F \frac{d_i^2}{(\lambda - k_i)^2}, \quad (2.15a)$$

$$V(\lambda) - V_0 = \sum_{i=1}^F \frac{d_i^2 (\lambda - \frac{1}{2} k_i)}{(\lambda - k_i)^2}. \quad (2.15b)$$

Figure 3 shows a sketch of the functions  $\Delta^2(\lambda)$  and

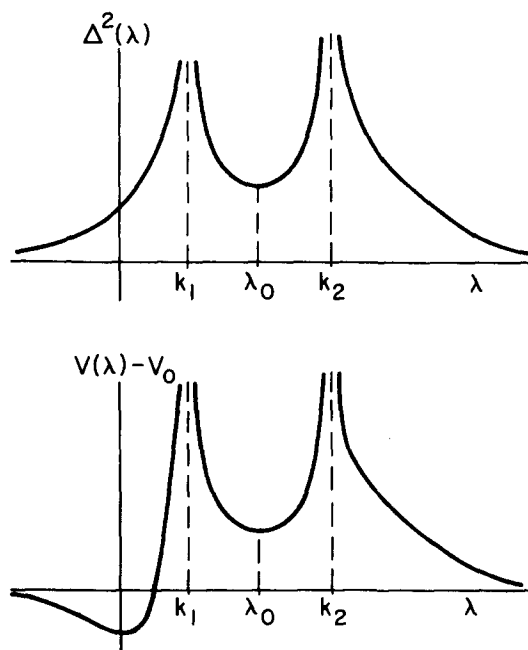


FIG. 3. Qualitative sketch of the functions  $\Delta^2(\lambda)$  and  $V(\lambda)$  defined by Eq. (2.15), for  $F=2$ .

$V(\lambda) - V_0$  [defined by Eq. (2.15)] for  $F=2$  and for the case that the initial point  $\mathbf{a}$  is close enough to the minimum of the potential for both eigenvalues of the force constant matrix  $k_1$  and  $k_2$  to be positive. Consistent with the discussion in Sec. II A, if the step size  $\Delta$  is sufficiently large, there will be four roots to the equation

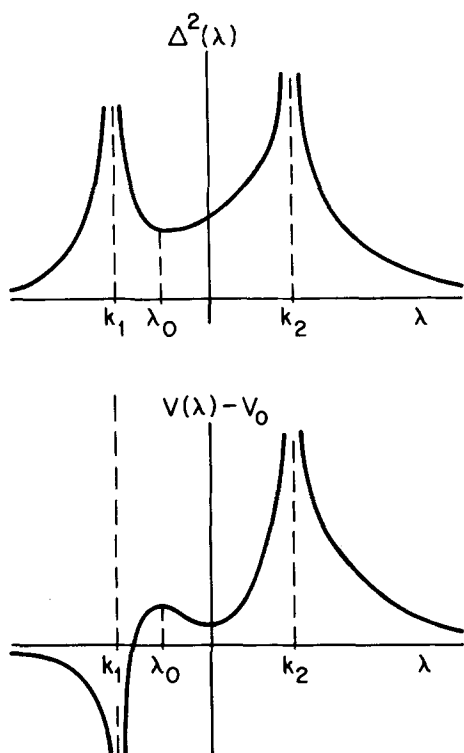
$$\Delta^2 = \Delta^2(\lambda), \quad (2.16)$$

i. e., four extrema of the potential. Varying the step-size  $\Delta$  varies the values of  $\lambda$  that satisfy Eq. (2.16), and we wish to choose the smallest (i. e., safest) value of  $\Delta$  for which there are still four roots to Eq. (2.16). This value of  $\Delta^2$  is clearly the local minimum of the function  $\Delta^2(\lambda)$  in Fig. 3, and the corresponding value of  $\lambda$  is  $\lambda_0$ , as indicated in the figure. One can easily show that  $\lambda_0$  also corresponds to the local minimum of  $V(\lambda)$  (cf. Fig. 3), and that  $V(\lambda_0) - V_0$  is positive, i. e., the step  $\Delta\mathbf{x}$  generated by choosing  $\lambda = \lambda_0$  is indeed uphill.

As one moves away from the absolute minimum of the potential toward the saddle point of the potential surface, the lowest eigenvalue of  $\mathbf{K}$  will become negative—this is the imaginary frequency corresponding to the reaction coordinate at the transition state—and the value  $\lambda_0$  can become negative. Figure 4 sketches the form of the functions  $\Delta^2(\lambda)$  and  $V(\lambda) - V_0$  for this case. One can show that in this case  $\lambda_0$  is a local maximum of  $V(\lambda)$ , as indicated in Fig. 4, and will thus not produce the desired step.  $\lambda=0$  does, however, correspond to a local minimum of  $V(\lambda)$  and is the choice in this case. For  $\lambda=0$  the increment  $\Delta\mathbf{x}$  of Eq. (2.12) is

$$\Delta\mathbf{x} = -\mathbf{K}^{-1} \cdot \mathbf{D}, \quad (2.17)$$

which is recognized as the Newton-Raphson step and known to be the most efficient choice once one is close enough to the saddle point.

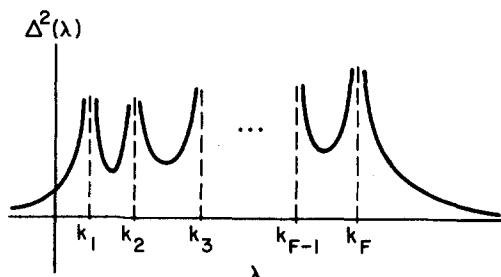
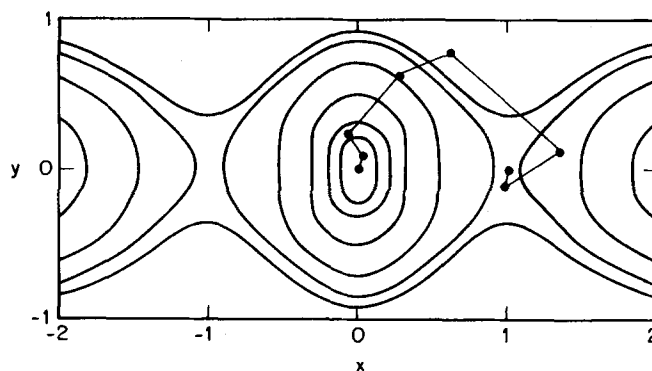
FIG. 4. Same as Fig. 3 except for the case  $k_1 < 0$ .

To summarize, the step  $\Delta x$  for walking uphill to a transition state from the minimum of the potential surface is given by Eq. (2.12), where  $\lambda = \lambda_0$  if  $\lambda_0 > 0$ .  $\lambda_0$  is the local minimum of the function  $\Delta^2(\lambda)$ , i.e., the root of the equation

$$\frac{d}{d\lambda} \Delta^2(\lambda) = -2 \sum_{i=1}^F \frac{d_i^2}{(\lambda - k_i)^3} = 0. \quad (2.18)$$

If  $\lambda_0 < 0$ , then one takes  $\lambda = 0$ . In practice the length of the step  $\Delta x$ ,  $\Delta^2(\lambda_0)$ , determined in this manner may be overly conservative, i.e., smaller than necessary, or unreasonably large, and in both cases we use the direction of the vector  $\Delta x$  but scale it to obtain a more reasonable step size.

For the general case  $F > 2$ , the function  $\Delta^2(\lambda)$  will have  $F-1$  local minima (cf. Fig. 5), and the normal prescription is to choose  $\lambda$  to be the smallest root of Eq. (2.18). As will be seen in some of the following examples,

FIG. 5. Sketch of the function  $\Delta^2(\lambda)$  for an arbitrary number of degrees of freedom  $F$ .FIG. 6. Contour plot of the two dimensional potential surface of Eq. (3.1). The points are the steps taken in walking from the minimum at  $(x, y) = (0, 0)$  to the transition state at  $(x, y) = (1, 0)$ .

though, it is sometimes possible to find other transition states by following other roots of Eq. (2.18).

### III. APPLICATIONS

As a first example, the two-dimensional model potential

$$V(x, y) = (a - by^2)x^2 e^{-x^2} + \frac{c}{2}y^2 \quad (3.1)$$

was studied. The minimum of the potential is located at  $(x, y) = (0, 0)$  and the two symmetrically placed transition states are located on the  $x$  axis at  $(x, y) = (\pm 1, 0)$ . To provide a severe test for the algorithm, the constants  $a$ ,  $b$ , and  $c$  were chosen so that at the potential minimum the eigenfrequency of the  $y$  direction is less than that for the  $x$  direction, and the initial step was taken in predominantly the  $y$  direction. (Because of symmetry the potential has a vanishing gradient in the  $x$  direction along the  $y$  axis, so an initial step in *exactly* the  $y$  direction will never lead to steps in other than the  $y$  direction.) The results of the calculations are shown in Fig. 6, and they illustrate the power of the algorithm: starting at the potential minimum and in essentially the wrong direction, the method marches in an efficient manner to the saddle point.

The second example examined was the vinylidene-acetylene isomerization,  $H_2C=C : \rightarrow HC \equiv CH$ . The transition state for this reaction has been studied by Poppin-

TABLE I. Geometries for vinylidene-acetylene rearrangement.<sup>a</sup>

Vinylidene	Perturbing step	Transition state
$r_1 = 2.48688$	2.48768	2.38823
$r_2 = 2.05224$	2.05224	2.71439
$r_3 = 2.05224$	2.05224	2.04870
$\theta_1 = 121.4^\circ$	$121.4^\circ$	$52.73^\circ$
$\theta_2 = -121.4^\circ$	$-121.8^\circ$	$-178.158^\circ$
$E = -73.53956$	$-73.53955$	$-73.48891$

<sup>a</sup>All values are in atomic units.

TABLE II. Geometries for formaldehyde rearrangement and dissociation.<sup>a</sup>

Formaldehyde	Pert. step for dissoc.	Pert. step for isom.	Disso. tr. st.	Isom. tr. st.
$r_1 = 2.30629$	2.30629	2.30629	2.26561	2.45074
$r_2 = 2.09716$	2.09716	2.07000	2.12082	2.12532
$r_3 = 2.09716$	2.09716	2.07000	2.90372	2.27089
$\theta_1 = 123.442^\circ$	123.442°	121.442°	156.648°	117.072°
$\theta_2 = 123.442^\circ$	122.442°	122.942°	+107.927°	-57.962°
$E = -109.02436$	-109.02430	-109.02374	-108.79256	-108.80808

<sup>a</sup>All values are in atomic units.

ger<sup>5</sup> and Muller and Brown<sup>6</sup> using other search techniques, and it thus provides a useful comparison test for the present method. Here, the starting geometry was chosen to be vinylidene and the initial step was taken along the direction of the lowest eigenfrequency. The energy evaluations were performed at the STO-2G level, using the values tabulated by Pople *et al.*<sup>8</sup> The minimum and transition state obtained from the perturbing state are given in Table I. An analytic first derivative program was used to generate the gradients, and the Hessian (i.e., second derivative matrix) was obtained from these by finite differencing.

The transition state was reached after eight increments, and agrees to all significant figures with those of Poppinger.<sup>5</sup> By way of comparison, the norm minimization method used by Poppinger required a reasonable guess at the transition state geometry and, in the most favorable case, 21 gradient evaluations starting from that guess. Our present calculations actually required more than 21 gradient evaluations since we determined the second derivative matrix  $\mathbf{K}$  by finite differencing the gradients. The purpose of this paper and these example calculations, however, is to look ahead to the time that one has available the computational methodology for the direct (i.e., analytic) evaluation of second derivatives,

and the point is that with the second derivative matrix, as well as the gradient, one can find transition states with considerably fewer steps. (Since it will undoubtedly require more computer time to evaluate first and second derivatives than just the first derivatives, though, one will have to weigh the trade off of fewer steps with more computer time per step.) This example illustrates the other obvious advantage of this algorithm, namely that a chemically intuitive starting point is not required to reach the transition state. This advantage would be especially pronounced in more complex molecules in which chemical intuition would fail to predict an adequate initial step, and there would be no stable systematic way to search for a transition state. Other techniques, such as the constrained simplex optimization,<sup>6</sup> are not competitive with the present Lagrange multiplier technique in terms of accuracy and efficiency.

For the last example, the potential surface for  $\text{H}_2\text{CO}$  was examined at the STO-2G level to see if the present technique could predict both the dissociative transition state  $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$  and the isomerization transition state  $\text{H}_2\text{CO} \rightarrow \text{HCOH}$ .<sup>9</sup> In this instance, slightly different perturbing steps were taken away from the minimum geometry and different eigenfrequencies followed along the ascent path. The values at the minimum, transition

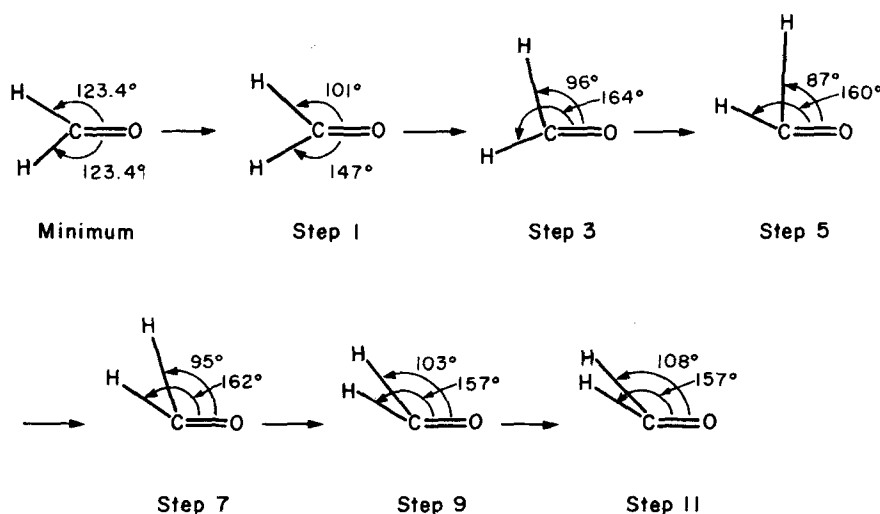


FIG. 7. Geometries for various steps in walking from the formaldehyde minimum on the potential surface to the transition state for dissociation ( $\text{H}_2 + \text{CO}$ ).

states, and perturbing steps are shown in Table II.

By following the lowest lying acceptable root for  $\lambda$ , the dissociative transition state was reached first, since the eigenfrequency producing this state is initially lower in energy. For the isomerization transition state, the second lowest acceptable value was chosen, which eventually gave the second transition state. The dissociative transition state was achieved after 11 increments from the perturbing step, and the isomerization transition state after nine increments from the perturbing step. For the rearrangement reaction, four increments along the higher lying eigenfrequency were necessary before the lowest eigenfrequency started to decrease and the second and third lowest roots interchanged. Some of the intermediate steps are given in Figs. 7 and 8 for the dissociation and rearrangement processes, respectively. Generally speaking, both transition states are approached in qualitatively the same manner. The largest steps are taken initially in the movement of the hydrogen atoms around the heavy atom bond, and then the bond distances relax to the transition state values. Physically this behavior is reasonable since the potential surface is likely to be shallowest for changes in angular orientation.

These results indicate that this technique is both efficient and stable. Provided that the appropriate value of the Lagrange multiplier is chosen, different regions of the potential energy surface are sampled, which, in the case of  $\text{H}_2\text{CO}$ , led to another transition state. It should be emphasized that nothing in the present method ensures the existence of any transition state—this is impossible for any method—but it is also clear that the Lagrange multiplier technique provides a routine way of searching for transition states.

Finally, we note that second derivative information can also provide a more efficient way of following the reaction path from a transition state *downhill* to reactants or products. If one tries to follow the negative gradient vector itself, large oscillations about the de-

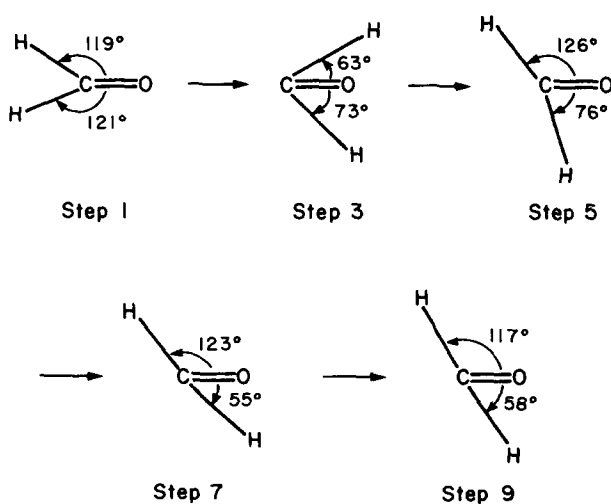


FIG. 8. Same as Fig. 7, except the transition state is for isomerization to  $\text{HCOH}$ .

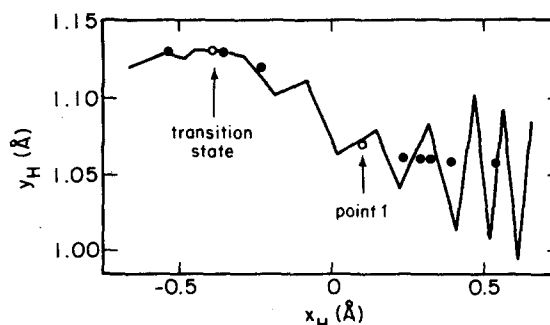


FIG. 9. Coordinates of the H atom in the  $\text{HNC} \rightarrow \text{HCN}$  isomerization. The solid line connects points obtained by simply following the gradient vector down from the transition state, and the solid points are the steps obtained by the present algorithm. Points to the right of "point 1" show the path obtained by starting at "point 1."

sired reaction path can result.<sup>10</sup> Present techniques to avoid these oscillations require additional gradient evaluations and smaller step sizes than otherwise necessary.

As an example, HCN isomerization was examined using the straightforward gradient procedure and the presently proposed alternative, which is essentially the algorithm described above in reverse. The results are shown in Fig. 9. With the known transition state geometry as a starting point,<sup>9</sup> several steps along the steepest descent path were determined on both sides of the saddle point, and these do not display the instabilities of the gradient method. A more dramatic instance is provided farther "downhill" where the oscillations about the true path have been more pronounced. With the choice  $x_{\text{H}} = 0.075 \text{ \AA} \sqrt{\text{amu}}$  (point 1 in Fig. 9) several steps taken toward the HNC minimum effectively interpolate the oscillations in the gradient calculations. It appears likely, then, that the use of the second derivative information will also be useful in generating intrinsic reaction coordinates.

#### IV. CONCLUDING REMARKS

The algorithm described and illustrated above for finding transition states has several extremely desirable features: it is stable, efficient, and a good initial guess for the transition state geometry is not required (although such a guess would of course reduce the number of steps needed). Its practical application to complex systems of interest, however, requires efficient computer codes for the analytic evaluation of the second derivative matrix of the potential surface, but it appears that these will be readily available soon.

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