

## An Internal Coordinate Invariant Reaction Pathway

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In this work we show that some properties of a potential energy surface are not independent of the choice of the coordinate frame. So the reaction pathway often described as steepest descent way does not correspond to an invariant curve under coordinate transformations. We propose an internal intrinsic reaction pathway by using some quasi-dynamical considerations (like instantaneous internal acceleration). Our work precises the intrinsic-reaction coordinates of Fukui to any set of  $3N-6$  internal parameters. Finally, from the equations of motion we deduce the form of the normal reaction coordinates frame anywhere along the postulated reaction pathway.

**Key words:** Reaction pathway – Gradient and force constant matrix – Potential energy surface – Reaction coordinates.

### 1. Introduction

A lot of potential surface studies use the concept of reaction pathway, but this notion remains confused [1]. If everybody agrees with the fact that the reaction pathway is a curve on the potential energy surface which connects the reactants and the products through the transition point, and that this curve has no dynamical significance, the discussion is not closed concerning this concept. Commonly for many works [2] it is accepted that the reaction pathway follows the bottom of a valley. First Laidler and Murell show that any transition point must correspond to a minimax of first kind [3]. McIver and Komornicki summarize the minimal requirements for the transition point and the reaction pathway [4]. Later Stanton and McIver make some remarks concerning more complex saddle points (like monkey-saddles) and concerning the invariance of the force constant matrix at the transition point [5]. McCullough and Silver [6] show that the steepest descent way on potential energy surface is more useful for describing the reaction pathway

than the notion of minimum energy path [7]; the former way meets the requirement of kinkless curve given by Marcus [8]. Finally Fukui et al. [9] propose the intrinsic reaction coordinate in order to follow the reaction pathway by using the weighted cartesian coordinate frame.

In the present work we will try to define for any set of internal coordinate system the concept of reaction pathway and to clarify such a notion.

## 2. The Potential Energy Surface and the Internal Coordinate Systems

If  $N$  is the atom number of the chemical system of interest (the molecule or the supermolecule), the potential energy  $E$  may be expressed as a function of  $3N - 6$  [10] internal coordinates ( $\sigma_1, \sigma_2, \dots, \sigma_{3N-6}$ ) components of the vector  $\sigma$ ; thus,

$$E = E(\sigma). \quad (1)$$

In order to avoid a kink we assume that  $\sigma$  is continuous in the whole space domain [11]. Anywhere on the potential energy surface we can compute the gradient vector  $g_\sigma$  and the force constant matrix  $H_\sigma$  with respect to the internal coordinates  $\sigma$  [12]:

$$g_\sigma = \nabla_\sigma E_\sigma, \quad (2a)$$

$$H_\sigma = \nabla_\sigma \nabla'_\sigma E_\sigma, \quad (2b)$$

where the subscript  $\sigma$  indicates that the function or the operator is given in terms of the variables  $\sigma$ , and the superscript ' stands for the transposition operation.

Let us now change the coordinate frame and define a new set  $v$  related to  $\sigma$  by the transformation

$$\sigma = Pv \quad (3a)$$

or

$$v = P^{-1}\sigma. \quad (3b)$$

This expression is always valid for infinitesimal displacements although it may be nonlinear as well as nonorthogonal. According to the chain rule [13] the derivatives with respect to  $\sigma$  are bonded to those with respect to  $v$  by the relations:

$$g_v = P' g_\sigma, \quad (4a)$$

$$H_v = P' H_\sigma P. \quad (4b)$$

The  $g$ 's are vectors of  $3N - 6$  components; they correspond to the same direction in  $\sigma$  or  $v$  only if  $g_\sigma$  and  $g_v$  are connected to each other by the same transformation as a vector. Comparing Eq. (4a) to (3b) we find that to meet this requirement,  $P^{-1}$  must equal  $P'$ . That means  $\sigma$  and  $v$  coordinate frames are related by a unitary transformation:

$$P'P = E. \quad (5)$$

Similarly the  $H$ 's are tensors of  $(3N - 6) \times (3N - 6)$  components;  $H_s$  and  $H_v$  may be transformed to each other like a tensor only if we meet the same restriction [5]. Thus, if we want to define the reaction pathway as "the steepest descent way for going from the transition point to the reactants or to the products", the reaction pathway (which so follows the gradient direction) is not invariant according to any set of coordinates. Nevertheless the location of any stationary point remains the same; even if  $P$  is not a unitary transformation, Eq. (4a) shows that anywhere  $g_s$  is zero  $g_v$  is also zero. The points which characterize the reactants, the products (two absolute minima) or the transition structure (a minimax of first kind [3]) are invariant with respect to the coordinate frame. As an example, we show in Fig. 1 the steepest descent pathways for the collinear reaction  $D + HF \rightarrow DH + F$  [14] in the following coordinate systems:

$$s' = (R_{DH}, R_{HF})$$

$$v' = (Q_2, Q_1).$$

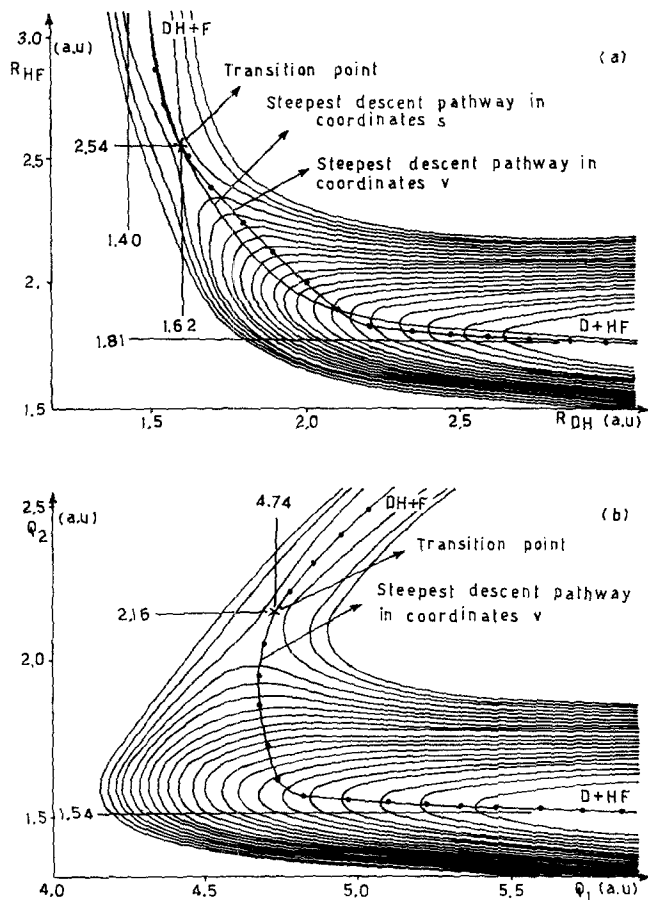


Fig. 1. Steepest descent pathway for the collinear  $D + HF$  reaction [13]. (a)  $E_s$  potential energy surface description; (b)  $E_v$  potential energy surface description.

$\sigma$  is an ordinary internal coordinate system and  $\nu$  is a coordinate system which diagonalizes the kinetic energy [15].

This figure shows that the steepest descent way is orthogonal to the isoenergy curves only when the potential energy surface is described in the same coordinate frame as the one used to build the steepest descent way.

As already shown by Stanton and McIver [5] the nature of any stationary point (minimum or minimax in particular) must be invariant in any kind of non-redundant coordinate frame ( $\det(P) \neq 0$ ); using Eq. (4b) it comes out,

$$\det(H_\nu) = \det(H_\sigma) \cdot \det^2(P). \quad (6)$$

As long as  $H_\sigma$  does not have zero eigenvalues the sign of the determinants of  $H_\sigma$  and  $H_\nu$  must be identical. Moreover we always can regard  $\nu$  as having evolved continuously from  $\sigma$ , then the number of negative or positive eigenvalues of  $H_\sigma$  and  $H_\nu$  must remain constant; that means that the nature of a stationary point is invariant under coordinate transformation. The existence of zero eigenvalues of the  $H$  matrix has been excluded by some authors [3–5] for interacting atoms or molecules. In the asymptotic region of dissociation such accident is nevertheless observed. In this case the  $H$  matrix can be partitioned and the last discussion remains valid for any part of  $H$  which does not correspond to zero eigenvalues.

### 3. The Internal Intrinsic Reaction Pathway

The internal acceleration of a system of points corresponds to the evolution capability of the system for a zero instantaneous velocity. In order to find the expression of the acceleration vector, let us write the equations of motion in terms of coordinates  $\sigma$ . Anywhere on the potential energy surface we can develop  $E(\sigma)$  in Taylor's series. We truncate the expansion to the second order assuming that any surface part close to a point of interest has a quadratic form. Then introducing the internal displacements  $s$  with respect to the expansion origin we have,

$$E(s) = E_0 + g'_\sigma s + \frac{1}{2} s' H_\sigma s, \quad (7)$$

with  $s = \sigma - \sigma_0$ .

The kinetic energy can be expressed in terms of internal displacements if we are using the Wilson's  $G$  matrix [16–17]:

$$2T = \dot{s}' G_\sigma^{-1} \dot{s}. \quad (8)$$

According to Eq. (7) and (8), the Lagrangian equation

$$\frac{d}{dt} \frac{\partial T}{\partial \dot{s}} + \frac{\partial E}{\partial s} = 0$$

becomes:

$$G_\sigma^{-1} \ddot{s} + g_\sigma + H_\sigma s = 0,$$

or, left multiplying by  $G_o$ , we have

$$\ddot{s} + G_o g_o + G_o h_o s = 0. \quad (9)$$

Such an expression is invariant with respect to any set of coordinate frame because  $\ddot{s}$ ,  $G_o g_o$  and  $G_o H_o s$  are always transforming like vectors. Indeed from (8) and (9) we see that

$$G_v = P^{-1} G_o P^{-1'}. \quad (10)$$

Then Eqs. (4) and (10) give

$$G_v g_v = P^{-1} G_o g_o; \quad (11)$$

$$G_v H_v = P^{-1} G_o H_o P.$$

For an infinitesimal displacement from the origin of the potential energy expansion ( $s \rightarrow 0$ ) we can write

$$\begin{aligned} \ddot{s} &\cong -G_o g_o \quad \text{for } g_o \neq 0, \\ \ddot{s} &\cong -G_o H_o s \quad \text{for } g_o = 0. \end{aligned} \quad (12)$$

If we start at the transition point we can define a unique curve with respect to any set of coordinates but mass depending by following anywhere the direction given by  $\ddot{s}$ . Such a curve connects the transition point to the reactants and to the products. It is kinkless as long as  $s$  frame, potential surface  $E(s)$  and  $B$  matrix are continuous. Then this curve may be chosen as the reaction pathway. Near the reactant or the product points it corresponds to the nuclear vibrational motions and generalizes the ideas of Swanson [18]. Our reaction pathway definition is similar to the one of Fukui et al. [9]. They use as coordinates the  $3N$  weighted cartesian coordinates ( $q$ ) instead of the  $3N - 6$  internal ones ( $s$ ). In such a case  $G_q$  is the unity matrix  $E$  and  $\ddot{q} = -g_q$ . We may then follow the  $-g_q$  direction. The main advantage of our purpose is to propose a general way to follow the intrinsic reaction coordinate of Fukui in any set of  $3N - 6$  internal coordinates. This paper may also be considered as a more simple approach to the reaction pathway problem compared to the work of Tachibana and Fukui [23] who are using differential geometry.

Practically to find the reaction pathway we will apply the following algorithm:

(1) Starting from transition point  $s_{\neq}$  we do a small step towards the reactants (or towards the products) in the eigendirection  $K^*$ , which corresponds to the negative eigenvalue of the  $GH$  product; so we are leaving the stationary point. The first displacement is given by

$$s_{\pm}^{(0)} = s_{\neq} \mp \frac{\varepsilon^2 K^*}{(K^{*'} K^*)^{1/2}}, \quad (13)$$

where the scalar  $\varepsilon^2$  stands for an infinitely small quantity and the product  $(K^{*'} K^*)^{1/2}$  is used in order to normalize each step at the value of  $\varepsilon^2$ .

(2) From the new point  $s_{\pm}^{(0)}$  we follow down the direction defined by the vector  $-Gg$ ; thus we have

$$s_{\pm}^{(i+1)} = s_{\pm}^{(i)} - \frac{\epsilon^2(Gg)_i}{(g'G'Gg)_i^{1/2}}. \quad (14)$$

(3) We stop the search if the gradient norm  $(g'g)^{1/2}$  is sufficiently close to zero or if the current energy tends to the energy of the reactants or to that of the products.

The first step implies the problem of diagonalizing the  $GH$  matrix at a stationary point. If both  $G$  and  $H$  are symmetrical matrices their product is in general unsymmetrical. The common diagonalization processes (Jacobi, Givens–Householder, . . .) are unallowed. As coordinates which diagonalize  $G$ , give also a diagonal form to the kinetic energy (see Eqs. (8) and (10)), it comes out that  $G$  is a positive defined matrix [19]. In such a case  $G^{1/2}$  matrix can be easily found by:

$$G^{1/2} = U\lambda^{1/2} \quad (15)$$

where  $\lambda$  stands for the diagonal matrix of the  $G$  eigenvalues and  $U$  stands for the square matrix of the  $G$  eigenvectors.

As usually done [20] we are now able to define a similarity transformation in order to diagonalize the  $GH$  product [21]. Multiplying  $GH$  left by  $G^{-1/2}$  and right by  $G^{1/2}$  we find for the symmetrical matrix ( $H_R$ ),

$$H_R = G^{1/2}HG^{1/2}. \quad (16)$$

This matrix has  $Y$  as eigenvectors and  $\Lambda$  as eigenvalues if

$$Y'H_R Y = \Lambda, \quad (17)$$

with

$$Y'Y = E.$$

Using the current notation [16–22] the eigenvectors  $L$  of  $GH$  become

$$L = G^{1/2}Y \quad (18a)$$

and

$$L^{-1} = K = Y'G^{-1/2}. \quad (18b)$$

In fact the similarity transformation corresponds to the definition of a new coordinate frame  $R$  such that

$$R = G^{-1/2}s, \quad (19)$$

in which set we write the matrix  $G_s H_s$ , by applying Eq. (4b) and we get the expression (16).

The present algorithm applied to the earlier mentioned example D+HF [13] gives as reaction pathway that of Fig. 1b (or the corresponding dotted line on Fig. 1a). In such a case we can easily verify that  $g_v$  must correspond to the same direction as  $G_s g_s$ .

Finally, one should not confuse the present definition of the reaction pathway with any possible trajectory (in dynamical meaning). In fact we exclude from our considerations the rotation of the whole system: as coriolis coupling terms exist, the vector  $\dot{s}$  is not free from rotational influence [22]. Moreover at any step of our algorithm we keep (artificially) the instantaneous velocities to zero. In the dynamical process we have:

$$\ddot{s}^{(i+1)} = -(Gg)_i$$

if

$$\dot{s}^{(i+1)} = \dot{s}^{(i)} - (Gg)_i t \quad (20a)$$

and

$$s^{(i+1)} = s^{(i)} + \dot{s}^{(i)} t - (Gg)_i \frac{t^2}{2} \quad (20b)$$

instead of Eq. (14). That means that  $\dot{s}^{(i)}$  always remains zero.

#### 4. The Normal Reaction Coordinates Frame

The  $G_s g_s$  vector defines anywhere on the internal intrinsic reaction pathway only one direction in the  $3N - 6$  dimensional coordinate space. Our purpose is now to find the  $3N - 7$  remaining space directions in order to have at our disposal a complete set of coordinates. So let us write Eq. (9) in the frame  $R$  defined by Eq. (19); it comes out from Eqs. (4a), (4b), (9), (16) and (19),

$$\ddot{R} + g_R + H_R R = 0; \quad (21)$$

by applying Eq. (17) we find

$$\ddot{R} + g_R + Y \Lambda Y' R = 0. \quad (22)$$

Left multiplying by  $Y'$  we can write:

$$\ddot{Q} + g_Q + \Lambda Q = 0, \quad (23)$$

where

$$Q = Y' R \quad (24)$$

$$g_Q = Y' g_R.$$

As  $\Lambda$  is a diagonal square matrix, Eq. (23) corresponds to a set of  $3N - 6$  uncoupled second order inhomogeneous differential equations and the  $Q$ 's define a normal coordinate frame which at any stationary point becomes the normal vibrational coordinates. Further as a unitary transformation ( $Y$ ) connects the  $Q$  and  $R$  frame the directions  $g_Q$  and  $g_R$  are identical and as the kinetic energy has a diagonal form in  $Q$  frame ( $2T = \dot{Q}' Q$ ) we easily understand why Fig. 1b corresponds to the general intrinsic reaction pathway.

Close to any stationary point as we follow one of the  $G_s H_s$  eigendirections, the  $g_Q$  components are all zero except one, that which corresponds to the reaction

pathway. Such a constraint remains valid anywhere on the reaction pathway as long as the reaction pathway follows the bottom of a valley. If the potential energy surface does not permit to satisfy this requirement the reaction pathway directions (defined by  $-g_Q$ ) may have more than one nonzero components. At this time  $g_Q$  does not remain eigenvector of  $H_Q$ ; nevertheless the corresponding direction may be kept as reaction pathway definition.

## 5. Conclusion

Using any set of internal coordinates for a chemical system, we may, by a first investigation of the potential energy surface, determine the location and the nature of stationary points, and consequently the activation barriers and the reaction energy.

If further we want to characterize the reaction pathway, rather than following the energy gradient with respect to the preceding coordinate set, we may use the concept of internal acceleration. Starting at the transition state, we let evolve the internal coordinates at a zero velocity, taking account of the masses of the different particles. Along the reaction pathway so defined we can find a set of normal coordinates, each associated with a local normal mode of motion. The reaction process itself corresponds to one particular normal mode of motion, provided that the gradient potential vector (in terms of normal coordinates) has one nonzero component along the intrinsic reaction pathway.

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