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Reaction Path Hamiltonian Based on a Reaction Coordinate and a Curvature Coordinate

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Keywords
Atom reactions, Hydrogen reactions, Vector calculus

Disciplines
Chemistry

Comments

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Reaction path Hamiltonian based on a reaction coordinate and a curvature coordinate

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We propose a reaction path-based Hamiltonian in terms of the reaction coordinate, the curvature coordinate, the remaining $3N-8$ transverse normal coordinates (whose directions are orthogonal to the path tangent and curvature vectors), and their conjugate momenta, for an $N$ atomic reaction system. The $3N-8$ transverse vibrational modes are independent of the motion along the reaction path, although they have coupling terms with the curvature direction in the harmonic approximation. A two-dimensional plane determined by the path tangent and curvature vectors is termed the "reaction plane." We introduce a function that estimates changes of the reaction plane along the reaction path, and analyze the reaction path based on this function for an abstraction reaction, $\text{CH}_3+\text{H}_2\rightarrow\text{CH}_4+\text{H}$. The scheme proposed here should be effective when a reaction path has a sharply curved region. © 1996 American Institute of Physics. [S0021-9606(96)02008-2]

I. INTRODUCTION

Within the Born–Oppenheimer approximation, a chemical reaction may be reduced to a dynamical process of nuclei on the (multidimensional) adiabatic potential energy surface. The knowledge of an entire potential energy surface provides the information necessary to obtain all features of the reaction dynamics. However, even with modern computational technology, it is impossible to determine an entire potential energy surface for more than a small number of dimensions. Therefore, theoretical chemists have devised reaction path-based models for dynamics calculations with an expectation that at low energies a reaction may proceed in a local region in the vicinity of the reaction path on the surface. In a pioneering work, a reaction path-based "natural collision coordinate system" was applied to a study of the (two-dimensional) collinear collision reaction, $\text{A+BC}\rightarrow\text{AB}+\text{C}$, by Marcus,1 Miller, Handy, and Adams2 extended this scheme to a multidimensional reaction of an $N$-atomic system, and derived a reaction path Hamiltonian based on a reaction coordinate and $3N-7$ normal coordinates, whose directions are orthogonal to the reaction path. The reaction path itself was rigorously defined by Fukui3 as the steepest descent path (or minimum energy path: MEP) in mass-weighted Cartesian coordinates starting from the transition state (TS) down to products and back to reactants,4 and the term, intrinsic reaction coordinate (IRC), was introduced to denote a curvilinear length along this MEP. When the $3N-7$ transverse vibrations can be regarded as adiabatic, a multidimensional dynamical process may be reduced to a one-dimensional process with an accompanying $3N-7$ dimensional harmonic bath. Truhlar and co-workers5 have developed a highly successful variational transition state theory based on this scheme.

A difficulty with the reaction path model occurs due to the curvature of the path. In a region where the reaction path is sharply curved, the reaction system should deviate considerably from the MEP due to an internal centrifugal force. This deviation leads to the loss of vibrational adiabaticity, and some energy may be transferred to vibrational modes which couple strongly with the reaction path (vibrational excitations). Kato and Morokuma6 discussed the mechanism of energy disposal along the reaction path based on the projection of the curvature vector onto $3N-7$ normal vibrational modes. Miller and Schwartz7 proposed a division of the reaction path Hamiltonian into a "system" of the reaction coordinate and modes strongly coupled to it, plus a "bath" of more weakly coupled modes. Truhlar and co-workers8 have extensively considered the effect of path curvatures on reaction path-based dynamics methods.

In the transfer of a light atom between two heavy centers, tunneling is very important. In such heavy–light–heavy systems, the reaction path is sharply curved in the TS region, making it difficult to estimate the tunneling contributions based on a one-dimensional reaction path model. For such systems, Miller and Carrington9 proposed a two-dimensional reaction surface model, in which the reaction proceeds on a two-dimensional surface determined by two reaction coordinate-like degrees of freedom (selected by chemical intuition) that can undergo arbitrarily large amplitude motions, with $3N-8$ degrees of freedom as bath modes, and derived a reaction surface Hamiltonian. This reaction surface was defined by minimizing the potential energy for fixed values of the two chosen reaction coordinates. In this scheme, the reaction in question becomes equivalent to a collinear atom–diatom reaction. Alternatively, for such a sharply curved reaction path system, Miller et al.10 proposed a "diabatic reaction path Hamiltonian" based on a straight-line (i.e., least motion) path that interpolates linearly between equilibrium reactant and product geometries of the molecular system. In this Hamiltonian, curvature coupling terms are absent, although terms that are linear in the normal coordinates appear in the potential energy.

Recently, we have implemented the dynamic reaction path (DRP) method11–14 into the electronic structure program package, GAMESS,15 and proposed14 two methods to describe the DRP based on the MEP: In the first method
(DRP-MEP), any point is expressed in terms of the IRC and the distance from the MEP; in the second method (DRP-MEPc), any point is expressed in terms of the IRC, the curvature coordinate (displacement in the negative of the IRC curvature vector), and the distance from the two-dimensional “reaction plane” determined by the IRC tangent and curvature vectors. This second method was proposed based on the fact that the 3N–8 dimensional space orthogonal to the IRC and its curvature directions should be independent of the motion along the MEP. However, the reaction plane defined here may be a function of the reaction coordinate. To analyze the stability of this reaction plane, we introduced a function that estimates changes of the basis vectors of the reaction plane, i.e., normalized path tangent and curvature vectors, along the MEP. In an application to the reaction H2CS→H2+CS, it was verified that the MEP can be separated into regions in which a reaction plane is almost stable (constant); in each such region, the centrifugal force makes the reaction system deviate strongly from the MEP in the direction of the negative of the curvature vector, with accompanying small deviations in the 3N–8 bath vibrational modes.

In this paper, we discuss the physical meaning of the DRP-MEP, scheme in detail, and derive the reaction path Hamiltonian based on this coordinate system. Then, as an example, the MEP for an abstraction reaction, CH3+H2 →CH3+H, is analyzed from the viewpoint of the reaction plane.

II. REACTION PATH HAMILTONIAN

For a collinear triatomic reaction, A+BC→AB+C, Marcus1 introduced the natural collision coordinate system which passes from coordinates appropriate to reactants to coordinates appropriate to products, and derived the classical Hamiltonian based on this coordinate system as,

$$H(s,p_s,Q,P) = \frac{p_s^2}{2(1 + Q\kappa(s))^2} + V(s) + \frac{1}{2} p^2 + \frac{1}{2} \lambda(s)Q^2.$$  

Here, s and ps are the reaction coordinate and its conjugate momentum, respectively; Q and P are the (transverse) vibrational coordinate and its conjugate momentum, respectively; κ(s) and λ(s) are the reaction path curvature and the harmonic force constant at s, respectively; V(s) is the potential energy along the MEP. Note that the positive direction of Q is taken to be on the convex side of the reaction path, and that the harmonic approximation has been incorporated into the potential about the reaction path. As is shown in Eq. (1), s and Q are coupled through the curvature κ(s) in the first term. When a reaction path is almost straight [i.e., κ(s) is nearly zero], these two motions can be treated separately, and the transverse vibration should be adiabatic. On the other hand, when the reaction path is sharply curved [i.e., κ(s) becomes large], their coupling becomes strong. The force in the Q direction is

$$-\frac{\partial H}{\partial Q} = -\lambda(s)Q + \frac{\kappa(s)p_s^2}{(1 + Q\kappa(s))^3}.$$  

The first term corresponds to a force caused by a harmonic potential, and the second to a centrifugal force due to the curve of the reaction path. Note that, in this simple collinear case, there is only one transverse vibrational mode, and the direction of this vibration coincides with the direction of path curvature (the direction of the internal centrifugal force).

Miller, Handy, and Adams2 extended this two-dimensional coordinate system to a general multidimensional reaction. Taking into account that any point on the MEP corresponds to a minimum in directions orthogonal to the reaction path, they derived the reaction path Hamiltonian in terms of s, ps, and transverse normal coordinates and their conjugate momenta, {Qk,Pk} [k=1,...,F−1 (F = 3N−6 is the number of vibrational degrees of freedom of the nonrotating N-atom system)] for total angular momentum J=0 as,

$$H(s,p_s,{Q_k,P_k}) = \left[ p_s - \sum_{k,l} Q_k P_l B_{k,l}(s) \right]^2 + V(s) + \sum_k \left[ \frac{1}{2} p_k^2 + \frac{1}{2} \lambda_k(s)Q_k^2 \right].$$  

Here, λk(s) is a harmonic force constant for the kth mode, B_{k,l}(s) is a coupling element between Q_k and Q_l, and B_{k,0}(s) is a coupling element between Q_k and s (motion along the MEP). These coupling elements are defined as
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\[ B_{k,j}(s) = \left( \frac{dL_k(s)}{ds} \right)' \cdot L_j(s), \]

(4)

\[ B_{k,F}(s) = \left( \frac{dL_k(s)}{ds} \right)' \cdot v(s), \]

(5)

where \( L_k(s) \) and \( v(s) \) denote the \( k \)th normal mode vector and the normalized path tangent vector at \( s \), respectively. The transverse vibrational modes, \( \{ L_1(s), \ldots, L_{F-1}(s) \} \), can be obtained as eigenvectors of the Hessian matrix (force constant matrix in mass-weighted Cartesian coordinates) at \( s \), from which infinitesimal translations, rotations, and \( v(s) \) have been projected out. Due to the orthogonality of the set \( \{ L_1(s), \ldots, L_{F-1}(s), v(s) \} \), \( B_{ij}(s) = -B_{ji}(s) \). Using this relation, Eq. (5) becomes \( B_{k,F}(s) = -[v^{(1)}(s)]' \cdot L_k(s), \)

(6)

where

\[ v^{(1)}(s) = \frac{dv(s)}{ds}. \]

(7)

Since \( v^{(1)}(s) \) is a curvature vector, and its magnitude is the scalar curvature \( \kappa(s) \), \( B_{k,F}(s) \) corresponds to a curvature component in the direction of \( L_k(s) \) (the negative sign in Eq. (6) reflects the fact that the positive direction of \( v^{(1)}(s) \) is toward the concave side). In this scheme, all transverse vibrational modes have a coupling with \( s \) along the MEP [cf. Eq. (1)]. Large values of \( B_{k,F}(s) \) produce a large centrifugal force in \( L_k(s) \), leading to a large deviation from the path in this direction. Miller and Schwartz \( ^7 \) divided the reaction path Hamiltonian into a system consisting of the reaction coordinate and modes strongly coupled to it, plus a bath of more weakly coupled modes based on the magnitude of \( B_{k,F}(s) \).

Kato and Morokuma \( ^6 \) discussed the energy disposal mechanism along the reaction path based on \( B_{k,F}(s) \).

Here, we propose an alternative extension of a natural collision coordinate system. Natural collision coordinates are composed of a reaction coordinate and a curvature coordinate [i.e., a displacement in the negative direction of \( v^{(1)}(s) \)], since the direction of a transverse vibration coincides with a path curvature direction. In our extension, a curvature coordinate is taken as one degree of freedom (because an internal centrifugal force works only in the direction of a path curvature). Then, the reaction process is described in terms of a reaction coordinate \( s \), a curvature coordinate \( \rho \), and the remaining \( F-2 \) normal coordinates; the basis vectors are given as \( \{ L_1(s), \ldots, L_{F-2}(s), -v^{(1)}(s)/\kappa(s), v(s) \} \) and \( v^{(1)}(s) \) determine a two-dimensional plane (referred to as the reaction plane), as in the case of a collinear atom–diatom reaction. Associated with this plane is a \( F-2 \) dimensional vibrationally adiabatic space. These \( F-2 \) transverse normal vibrational modes can be obtained as eigenvectors of the projected Hessian matrix, \( \mathbf{K}_p(s) = (1 - \mathbf{P}(s)) \mathbf{K}(s) (1 - \mathbf{P}(s)) \), where \( \mathbf{K}(s) \) and \( \mathbf{P}(s) \) denote a Hessian matrix and a projector at \( s \), respectively. The projector \( \mathbf{P}(s) \) is defined as

\[ \mathbf{P}(s) = \sum_{i=F+1}^{F+6} \mathbf{L}_i(s) \cdot \mathbf{L}_i(s)' + v(s) \cdot v(s)' + [v^{(1)}(s) \cdot v^{(1)}(s)']/\kappa(s)^2, \]

(8)

where \( \mathbf{L}_i(s) \) (\( i = F+1, \ldots, F+6 \)) denote translational and rotational modes. As a result, the Hamiltonian can be written as,

\[ H(s, \rho, \rho, \mathbf{L}_i, \mathbf{L}_j, \mathbf{Q}_k, \mathbf{P}_k) \]

\[ = \frac{p_s^2}{2(1 + p\kappa(s))^2} + V(s) + \frac{1}{2} \rho^2 + \frac{1}{2} \lambda_{\rho}(s) \rho^2 + \sum_k \left| \frac{1}{2} P_k^2 + \frac{1}{2} \lambda_k(s) Q_k^2 + \lambda_{k,F-1}(s) \rho Q_k \right|, \]

(9)

where \( \rho \) and \( \rho \) are the curvature coordinate and its conjugate momentum, and \( \lambda_{k,F-1}(s) \) is an off-diagonal element of the force constant matrix \( (\partial^2 V(s)/\partial Q_k \partial \rho) \). Here, Coriolis coupling terms of the normal modes with each other have been neglected. In this scheme, there is a kinetic energy coupling between \( s \) and \( \rho \), and there is a potential energy coupling between \( Q_k \) and \( \rho \). The first four terms in Eq. (9) correlate with those in Eq. (1).
The above definition of reaction plane provides a way to derive a two-dimensional plane which may be important for the reaction dynamics in a $3N-6$ dimensional space. The deviation from the MEP due to a centrifugal force occurs within this plane (classical mechanical viewpoint) and the least motion path of the system, which may be related to a tunneling process, is located on this plane (quantum mechanical viewpoint). Since one objective of the MEP is to obtain a one dimensional curve from a multidimensional space, the reaction plane described here is a natural extension of the one-dimensional reaction path model. The more strongly the MEP curves, the more important the reaction plane description becomes.

If one expands the kinetic energy in Eq. (3) to lowest order in the couplings and neglects the Coriolis coupling terms of the normal modes with each other, the reaction path Hamiltonian may be reduced to

$$H(s,p_s,\{Q_k, P_k\}) = \frac{1}{2} p_s^2 + V(s) + \sum_k (\frac{1}{2} p_k^2 + \frac{1}{2} \lambda_k(s) Q_k^2 - p_k^2 B_k(s) Q_k).$$

(10)

In a similar manner, Eq. (9) can be reduced to

$$H(s,p_s,\rho_p,\{Q_k, P_k\}) = \frac{1}{2} p_s^2 + V(s,\rho) - \frac{1}{2} p_\rho^2 \kappa(s) \rho$$

$$+ \sum_k (\frac{1}{2} p_k^2 + \frac{1}{2} \lambda_k(s) Q_k^2 + \lambda_{k,F-1}(s) \rho Q_k).$$

(11)

In Eq. (10), all normal modes are influenced by the motion along the path due to the last term, $-p_k^2 B_k(s) Q_k$. When $B_k(s)$ is large, the deviation from the reaction path is expected to be large in the direction of $Q_k(s)$, and the corresponding anharmonic effects should be considered. On the other hand, in Eq. (11), a large deviation due to the internal centrifugal force may be expected only in the direction of $Q_k$ only couples directly with $\rho$. Then, beyond the harmonic approximation for this direction, the Hamiltonian should be rewritten as

$$H(s,p_s,\rho_p,\{Q_k, P_k\})$$

$$= \frac{1}{2} p_s^2 + \frac{1}{2} p_\rho^2 + V(s,\rho) - p_\rho^2 \kappa(s) \rho$$

$$+ \sum_k (\frac{1}{2} p_k^2 + \frac{1}{2} \lambda_k(s) Q_k^2 + \lambda_{k,F-1}(s) \rho Q_k),$$

(12)

where $V(s,\rho)$ denotes a two-dimensional adiabatic potential energy surface (reaction surface) corresponding to the reaction plane.

In a reaction plane scheme, the other $F-2$ modes are indirectly influenced through the potential coupling terms, $\lambda_{k,F-1}(s) \rho Q_k$. These indirect effects can be estimated by the coupling element $\lambda_{k,F-1}(s)$. This coupling mechanism may be examined using the Hessian matrix. In the coordinate system, $\{s,Q_1,\ldots,Q_{F-2}\}$, the Hessian is expressed as

$$B_{k,F}(s) = \frac{\lambda_{k,F}(s)}{(\partial V(s)/\partial s)}.\quad (14)$$

On the other hand, the Hessian in the present system, $\{s,\rho,Q_1,\ldots,Q_{F-2}\}$, is expressed as

$$\begin{pmatrix}
\lambda_1 & \cdots & 0 & \lambda_{1,F} \\
\vdots & \ddots & \vdots & \vdots \\
0 & \cdots & \lambda_{F-1} & \lambda_{F-1,F} \\
\lambda_{F,1} & \cdots & \lambda_{F-2,F} & \lambda_{F-2,F-1} & 0 \\
0 & \cdots & 0 & \lambda_{F-1,F} & \lambda_s
\end{pmatrix}.$$\quad (13)

Note that the relation between $B_{k,F}(s)$ and $\lambda_{k,F}(s)$ is, for $s$ \textsuperscript{4,6}

$$B_{k,F}(s) = \frac{\lambda_{k,F}(s)}{(\partial V(s)/\partial s)}.$$\quad (14)

In analogy with Eq. (14), the relation between $\kappa(s)$ and $\lambda_{F-1,F}(s)$ is

$$\kappa(s) = \frac{\lambda_{F-1,F}(s)}{(\partial V(s)/\partial s)}.$$\quad (16)
TABLE I. Geometrical parameters at the reactants (R), the transition state (TS), the dividing points (DP,k=1,2,3), and the products (P) for the reaction CH$_3$+H$_2$→CH$_4$+H at the (a) UHF and (b) CASSCF levels. Notations for geometrical parameters are defined in Fig. 4. Bond lengths are in Å, angles in degrees.

<table>
<thead>
<tr>
<th></th>
<th>r$_{CH1}$</th>
<th>r$_{H1H2}$</th>
<th>r$_{CH3}$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) UHF</td>
<td></td>
<td></td>
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<tr>
<td>R</td>
<td>0.733</td>
<td>1.073</td>
<td>90.0</td>
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<tr>
<td>DP$_i$ (s=−0.65)</td>
<td>1.678</td>
<td>0.750</td>
<td>1.076</td>
<td>100.6</td>
</tr>
<tr>
<td>TS</td>
<td>1.363</td>
<td>0.931</td>
<td>1.079</td>
<td>104.4</td>
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<tr>
<td>DP$_i$ (s=0.17)</td>
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<td>1.038</td>
<td>1.080</td>
<td>105.0</td>
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<td>DP$_i$ (s=0.80)</td>
<td>1.074</td>
<td>1.447</td>
<td>1.083</td>
<td>108.0</td>
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<tr>
<td>P</td>
<td>1.084</td>
<td>1.084</td>
<td>109.5</td>
<td></td>
</tr>
<tr>
<td>(b) CASSCF</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>0.753</td>
<td>1.093</td>
<td>90.0</td>
<td></td>
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<tr>
<td>DP$_i$ (s=−0.65)</td>
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<td>0.771</td>
<td>1.097</td>
<td>100.3</td>
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<td>TS</td>
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<td>104.1</td>
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<td>1.076</td>
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<td>1.103</td>
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<tr>
<td>P</td>
<td>1.104</td>
<td>1.104</td>
<td>109.5</td>
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</table>

III. VARIATION OF THE REACTION PLANE

As discussed in the previous section, when there is a large curvature region along the MEP, one may need to go beyond a one-dimensional reaction path model for dynamics calculations. Miller et al. proposed a reaction surface Hamiltonian in which the (two-dimensional) reaction surface is determined by minimizing the potential energy for fixed values of two reaction coordinates: Any point on the reaction surface corresponds to an energy minimum in a 3N−8 dimensional space orthogonal to the reaction surface. In our scheme, the reaction surface $V(s,p)$ is determined by the reaction plane [defined by unit vectors $v(s)$ and $-\nabla^{(1)}(s)/\kappa(s)$], which change along the MEP. When the MEP is characterized by only one reaction plane, the reaction becomes equivalent to a collinear atom–diatom reaction. However, in general, the MEP can have several reaction planes. Figure 1 shows a schematic illustration of the MEP with two reaction planes. For each reaction plane, a least motion path (LMP) that interpolates linearly between two boundary points may be determined as shown.

In those regions where there are rapid changes in the reaction plane, one expects that the reaction system will move away from this two-dimensional plane, in analogy with behavior expected in high curvature regions on a reaction path. In order to measure changes in the reaction plane, we introduced the vector $w(s)$.\(^{14}\)

$$w(s) = \frac{v^{(2)}(s)}{\kappa(s)} - \frac{v^{(1)}(s)\cdot v^{(2)}(s)}{\kappa(s)^3} v^{(1)}(s)$$

$$= \frac{v(s)^2 \cdot v^{(2)}(s)}{\kappa(s)} v(s),$$

(17)

where

$$v^{(2)}(s) = \frac{d^2 v(s)}{ds^2}.$$  

(18)

When the magnitude of $w(s)$ becomes large, the reaction plane changes drastically. Even when the reaction system deviates considerably from the MEP due to large path curvature, the deviation from the reaction plane should be small unless $|w(s)|$ becomes large.

IV. AN EXAMPLE: CH$_3$+H$_2$→CH$_4$+H

As a demonstration, the MEP of an abstraction reaction, CH$_3$+H$_2$→CH$_4$+H, was calculated with ab initio MO methods and was analyzed from the viewpoint of changes of the reaction plane. This reaction has been extensively studied, including the nature of the MEP.\(^{4(c),4(d),16}\) This MEP conserves $C_3v$ symmetry throughout. In this study, to examine the (nondynamic) electron correlation effects, the MEP was calculated by two methods, i.e., the unrestricted Hartree–Fock (UHF) method and the full-valence complete active space self-consistent field (CASSCF) method (nine electrons over nine orbitals in the active space), with the 6-31G(d,p) basis set. At both levels of calculation, the TS geometry was first optimized so that the largest component of the (Cartesian) gradient is less than $10^{-6}$ hartree/bohr, and the MEP was calculated, starting from the TS to reactant and to products, by the Runge–Kutta fourth order integration method with a step size of 0.005 bohr amu.\(^{12}\) The path tangent vector $v(s)$ was simultaneously determined for each calculated point on the MEP. These calculations were performed using the GAMESS program.\(^{15}\)

Next, $v^{(1)}(s)$ and $v^{(2)}(s)$ were calculated by numerical differentiation of $v(s)$ to determine a scalar curvature, $\kappa(s)$ (=$|v^{(1)}(s)|$), and $w(s)$ in Eq. (17), along the MEP. In these calculations, we have found that the $|w(s)|$ values calculated from the CASSCF-MEP were very scattered, despite very stringent MCSCF convergence, especially in regions where $\kappa(s)$ is small. This suggests difficulty in precisely locating the MEP at the CASSCF level in comparison with the HF level.\(^{17}\) Therefore, we used $v^{(1)}(s)$ and $v^{(2)}(s)$ calculated through numerical differentiation of $v(s)$ chosen from every ten sample points on the MEP (Δs=0.05 bohr amu\(^{12}\)) for the calculation of $w(s)$ along the CASSCF-MEP (every 30 points for small curvature regions near reactants and products side). Then, 10 (or 30) different sets of $\{w(s)\}$ calculated from 10 (or 30) different sets of $\{v(s)\}$ were combined in the profile.

Figure 2 shows changes in $\kappa(s)$ and $|w(s)|$ as a function of reaction coordinate, s, calculated along the UHF-MEP. Since some points near the TS deviate from the MEP, they have been removed. Before and after the TS (s=0), $\kappa(s)$ shows two large peaks. These large curvatures suggest that, in this reaction, a one-dimensional reaction path model is
likely to give a poor description of the dynamics. Before and after a peak in $\kappa(s)$, $|w(s)|$ becomes large (i.e., the reaction plane changes sharply); in particular, $|w(s)|$ changes very rapidly around $s=0.80$ bohr amu$^{-1}$. On the other hand, around a peak in $\kappa(s)$, the reaction plane seems stable. This relation between $\kappa(s)$ and $|w(s)|$, also observed for the H$_2$CS reaction,\textsuperscript{14} may be general.

Figure 3 shows changes in $\kappa(s)$ and $|w(s)|$ calculated along the CASSCF-MEP. Comparison of Figs. 2 and 3 illustrates that the nature of the CASSCF-MEP is almost the same as that of the UHF-MEP for this reaction.

In this reaction, the MEP may be divided into four regions; dashed vertical lines are drawn at the dividing points (DP$^1$, DP$^2$, and DP$^3$), and the products at the UHF and the CASSCF levels. The definition of coordinates is given in Fig. 4. Although bond lengths at the CASSCF level are slightly longer than those at the UHF level, they are qualitatively similar. In the conventional reaction path Hamiltonian approach,\textsuperscript{2} the curvature is related to a coupling between the motion along the MEP and the vibrational motions orthogonal to the reaction path. Baldridge et al.\textsuperscript{14b} examined the coupling element, $B_{k,k}(s)$ in Eq. (5), for this reaction, and showed that the curvature before the TS is related to the H1–H2 stretching motion, and the curvature after the TS is related to the C–H1 stretching motion. This result is supported by the geometries of DP$^2$: the H1–H2 bond length at DP$^2$ is almost the same as that in reactants R, and the C–H1 bond length at DP$^3$ is almost the same as that in products P. So, the second region (DP$^1$→DP$^2$) corresponds to bond cleavage of H1–H2, and the third region (DP$^2$→DP$^3$) corresponds to bond creation of C–H1. As is shown in Fig. 1, a LMP may be determined by connecting DP$^2$ and DP$^{k+1}$ linearly in mass-weighted Cartesian coordinate space. In other words, each DP$^2$ on the MEP is a turning point of the LMP, and so, it is convenient to give their geometries as characteristic points for an understanding of the reaction mechanism.

V. CONCLUSION

In this paper, we propose an alternative reaction path Hamiltonian in terms of a reaction coordinate, a curvature coordinate, and the remaining 3N−8 normal coordinates, plus momenta conjugate to these coordinates. The relation of this scheme to the conventional reaction path Hamiltonian by Miller et al. as well as to the natural collision coordinate model developed by Marcus is discussed. To evaluate the variability of a reaction plane determined by the path tangent and curvature vectors, an estimating function, $|w(s)|$, is introduced. This analysis is applied to the reaction, CH$_3$+H$_2$→CH$_4$+H, to illustrate that, while the reaction path curves sharply, the reaction plane is stable. So, in general, one should first separate the MEP into stable regions (reaction plane) determined by $|w(s)|$, and then examine the reaction surface $V(s,\rho)$ of each region in a wide range, especially for sharply curved regions.

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\textsuperscript{12}T. Taketsugu and T. Hirano (to be submitted).


17 Use of the Gonzalez–Schelegel second order algorithm or decreasing the MEP step size to 0.001 did not diminish the problem.